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A study of the gelation of air-setting refractory mortars

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A STUDY OF THE GELATION OF AIR-SETTING REFRACTORY MORTARS

by

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The undersigned, appointed by the Dean of the Graduate Faculty, have examined a thesis entitled "A Study of the Gelation of Air-Setting Refractory Mortars".

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ABSTRACT

One of the most common sources of concern among the manufacturers of air-setting refractory mortars is the tendency of the mortar to harden out of contact with air. Most of these manufacturers have worked on this problem in their plant laboratories, but very little has been published explaining the mechanism of this hardening and giving possible solutions.

The term "gelation" has been applied to the hardening of the mortars since, after storage, the mortar has the properties of a thixotropic gel. The purpose of this study was to investigate the problem from several different approaches and was (1) to determine the possible causes of gelation; (2) to determine which of these is the predominant factor; and (3) to develop ways and means by which the gelling could be retarded or eliminated completely.

A review of literature showed that certain information from investigators in other fields was applicable to the problem and the different types of electrodialysis cells used by previous workers were discussed.

A modified Vicat needle apparatus was used in this study to determine the workability of the mortars. Electrodialysis was used to remove the adsorbed ions from the clays and the possibility of determining quantitatively the

relative amounts of monovalent and polyvalent cations removed during the process was discussed.

Three basic mortar formulae were used in this investigation, each mix having some different materials present and each having its own gelling characteristics. The study was directed along the theory that the dry materials used play an important part in the hardening. Certain admixtures were tested and several were found to improve the workability after storage. The presence of additional sodium ions in the mortar was found to be helpful in overcoming the gelation but these tended to lower the refractoriness of the mortar.

A study was made of the base exchange capacities of the dry materials and the material with the highest base exchange capacity was found to contribute more to the gelation than did one without so many exchangeable cations. The flame photometer was employed to analyze the concentration of the alkaline ions in the effluents obtained during the electrodialysis of a clay and the results indicated that the peaks in the time-current curve of the dialysis may be indicative of the relative amounts of the two valence-type ions removed.

The effect of the mineral constituents of the clays used in the mortars was discussed. One of the clays was found to contain considerably more free silica than did the

other clay. This did not seem to have too great an effect on the hardening during the storage period. Opal was found to be present in one of the clays and differential thermal curves were given in an attempt to use this method to determine whether or not this mineral was present.

It was concluded that the gelation was not due to any one single factor but that the most predominant cause was the presence of polyvalent exchangeable cations adsorbed to the clay or other dry materials used in the mortars. The presence of free silica was found to cause some hardening, but this was deemed only a minor factor. The use of bentonite as a suspending medium in the mortar was found to be detrimental to the workability of the mortar as its high exchange capacity and high percentage of exchangeable magnesium was found to increase the gelation considerably.

CHAPTER I

THE PROBLEM AND DEFINITIONS OF TERMS

One of the most common sources of concern among the manufacturers of air setting refractory mortars who use sodium silicate as the bonding agent is the tendency of the mortar to harden out of contact with air. Most of these manufacturers have worked on this problem in their plant laboratories, but very little has been published explaining fully the mechanism of this hardening and giving possible solutions.

I. THE PROBLEM

Statement of the problem. It was the purpose of this study to investigate the problem from several different approaches and in this manner (1) to determine the possible causes of this hardening; (2) to determine which of these causes is the predominant factor; and (3) to develop ways and means by which this hardening can be retarded to a satisfactory degree or eliminated completely.

Importance of the study. If a sealed, metal container of this mortar is allowed to remain at room temperatures and not disturbed, the mortar will show tendencies of hardening within two to seven days. After about six weeks, the mass becomes very hard, but its moisture content is

about the same as when mixed. The material will usually regain its original consistency if it is placed in a mortar box and worked for from twenty to thirty minutes. The elimination of this characteristic of the mortar would be of great advantage to the manufacturers in the marketing of a more satisfactory product and to the consumer in that the mortar is ready to use upon receipt and does not require further processing.

II. DEFINITIONS OF TERMS

Refractory mortar. The term, "refractory mortars" as used in this paper is intended to refer to air setting refractory mortars composed generally of a base of calcined fireclay or raw flint clay, a plastic fireclay, and/or calcined diaspore clay, raw kyanite, silica or any other refractory material and from five to fifteen percent of sodium silicate added in liquid form. Under no circumstance will this term be applied to refractory mortars that utilize dry sodium silicate or any other bonding agent unless specifically noted.

Gelation. This term will be used to more accurately clarify the action taking place within the mortar during storage. The word "hardening" has been generally applied by the refractory industry, however, the gelation referred to by this paper is intended to signify the formation of a

two phase, liquid and solid, system in which both phases are continuous which owes its rigidity to a type of network structure.

Clay. The clay referred to in this study will be raw plastic fireclay from Callaway County, Missouri.

Effluents. This term will be used to describe the liquids obtained from the overflow of the electrode chambers during electrodialysis. These are sometimes referred to in the literature as the dialysates, the catholyte and anodolyte, but in this paper they will be referred to as the anode effluents and the cathode effluents to differentiate between the effluent obtained from the positive and negative electrode.

Workability. The workability of a refractory mortar will be referred to and should be interpreted as meaning the ease in which the material can be used. Hence, if the workability of a mortar is "good", its consistency is about the same as when it was manufactured. If the workability is poor, the mortar can not be applied satisfactorily to its intended uses and must have additional mixing.

III. ORGANIZATION OF STUDY

In order to report the findings of this study more effectively, the remainder of this paper has been broken down into four general topics and one chapter has been

assigned to each of these. Chapter II covers a review of the literature on all of the topics included in this study and a discussion of the limitations, if any, of these previous studies.

The third chapter has been devoted to an explanation of the experimental procedures and processes used. This should enable the reader to evaluate the equipment and methods used for any further work. Chapter IV lists all of the data obtained and the discussion of these results. Finally, the summary is given in Chapter V and the conclusions and final discussion is given therein.

CHAPTER II

REVIEW OF LITERATURE

I. SODIUM SILICATE

Due to the many uses of the soluble silicates, much has been written about them, but Vail's book[1] is by far the most comprehensive. His work includes a discussion of the manufacture, properties and industrial and non-industrial uses of the soluble silicates, so that it was not deemed advisable to include a discussion of these topics in this study, but it does seem necessary to discuss the constitution of these materials.

The silicates are marketed according to their sodium to silica ratio and the percent solids present. These two factors decide generally their properties and their uses. The most siliceous silicate available commercially as a liquid has a composition Na_2O: 3.90 SiO_2 and carries about 31 percent solids.[2] The most alkaline silicate marketed has a composition Na_2O: 1.60 SiO_2 with from 51 to 63 per-

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1 J. G. Vail, Soluble Silicates in Industry, (New York: The Chemical Catalog Company, Inc., 1928), 443 pp.

2 C. H. Jeglum, "The Properties of Soluble Silicates", Bulletin Number 1703, (Philadelphia, Pa., The Philadelphia Quartz Company, 1947), p. 5.

cent solids.[3]

There has been considerable discussion as to the exact constitution of these silicates, as regards to the manner in which the particles are present in solution. It is generally agreed that all commercial silicates marketed in liquid form are of a colloidal nature[4]. However, considerable experimentation has shown that these solutions are not wholly colloidal, but, as Vail states, "industrial silicate solutions are systems in which colloidal silica plays an important role. To attempt to interpret their behavior without taking this into account is to miss the meaning of some of the most important phenomena"[5].

Kohlrausch's work[6] on the conductivity of silicate solutions showed rather conclusively that colloidal silica was present in most of the solutions studied. His work was a study of silicates prepared by dissolving crystalline

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3 C. H. Jeglum, "The Properties of Soluble Silicates", Bulletin Number 1703, (Philadelphia, Pa., The Philadelphia Quartz Company, 1947), p. 6.

4 "Brands, Properties, Applications", Bulletin Number 17 - 1, (Philadelphia, Pa., The Philadelphia Quartz Company, 1947), p. 2.

5 Vail, op. cit., p. 17.

6 F. Kohlrausch, "On Solutions of Sodium Silicates: Especially Relating the Influence of Time on their Constitution", Zeitschrift für Physikalische Chemie, 12: 772-91, 1893.

metasilicates in water and sodium hydroxidex, and covered generally a range of concentrations from the metasilicate, Na_2SiO_3, to $Na_2O: 3.4SiO_2$. By comparing the conductivity of the metasilicate in very dilute solutions with comparable solutions of sodium chloride, sodium nitrate and sodium acetate, he noted that the former conducted the current better. As the concentration was increased, the conductivity decreased rapidly. His conclusions were that the high conductivity of the dilute solutions was due to hydrolysis, which supposedly converted the salt into silicic acid and sodium hydroxide.

R. W. Harman made a very complete study of the sodium silicates and stated in one of his early papers[7] that, at the beginning of his work, he rather doubted whether there were any definite sodium silicates other than Na_2SiO_3, since no conclusive evidence had been presented to show whether the higher silica-soda ratio materials were definite salts of mixtures of the metasilicate and silicic acid or caustic soda. Harman studied the constitution of the silicates using transport number experiments[8], measure-

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7 R. W. Harman, "Aqueous Solutions of Sodium Silicates; Part II. Transport Numbers", The Journal of Physical Chemistry, 30: 359, 1926.

8 Ibid, 359-68.

ment of the sodium ion activity[9], and measuring the degree of hydrolysis by determining the hydroxyl ion concentration[10].

A general survey of all of his work[11] indicates that only the 1:1 and 1:2 ratio silicates are definite salts and that above the 1:2 ratio, colloidal silica is present. The concentrated solutions are characterized by low conductivity, little or no hydrolysis, low sodium ion concentration and very high viscosity. His explanation of the form of silica present in these silicates was that it exists not wholly as a colloidal material but as crystalloidal silica. He further states that very concentrated solutions should be considered as colloidal electrolytes, since the silicate exists as a very complex aggregate. McBain and Salmon[12]

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9 R. W. Harman, "Aqueous Solutions of Sodium Silicates; Part III. Sodium Ion Activity", The Journal of Physical Chemistry, 30: 917-24, 1926.

10 R. W. Harman, "Aqueous Solutions of Sodium Silicates; Part IV. Hydrolysis", The Journal of Physical Chemistry, 30: 1100-11, 1926.

11 R. W. Harman, "Aqueous Solutions of Sodium Silicates; Part VIII. General Summary and Theory of Constitution. Sodium Silicate as Colloidal Electrolytes", The Journal of Physical Chemistry, 32: 44-60, 1928.

12 James W. McBain and C. S. Salmon, "Colloidal Electrolytes. Soap Solutions and their Constitution", The Journal of the American Chemical Society, 42: 426-60, 1920.

define a colloidal electrolyte as a "salt in which an ion has been replaced by a heavily hydrated polyvalent micelle that carries an equivalent sum-total of electrical charges and conducts electricity just as well or even better than the simple ion it replaces."

Main[13] studied the effect of the soda:silica ratio on the viscosity of the silicate solution and found that at low concentrations the change of viscosity with increasing silica content was not great. At higher concentrations, he found that the viscosity was much higher and he stated that these investigations seemed to indicate that a solution of concentration higher than 1:4 could not be prepared and still have the properties of a fluid.

II. GELATION OF SODIUM SILICATE

One of the most widely studied gels has been silica gel. It is easy to prepare and the properties it exhibits make it widely used in industry. The most popular method of preparation is by the addition of a weak acid to a sodium silicate solution to form a jelly-like precipitate. This is then thoroughly washed and dried for use as an adsorbent. In the petroleum industry, acetic acid is added

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13 V. R. Main, "The Viscosity of Aqueous Solutions of the Silicates of Soda", The Journal of Physical Chemistry, 30: 535-61, 1926.

to sodium silicates to produce highly viscous liquids to be used with drilling muds.

The addition of heavy metals salts to sodium silicate solutions has also been recognized for a long time as a method of precipitating gelatinous silicates. These masses are assumed to be mixtures of silicic acid and metallic silicates.[14] In 1911, this reaction was first used for chemical grouting by two Belgians, Lamaire and Dumont, who had trouble in waterproofing and bracing a salt mine shaft. Sodium silicate was added and shortly thereafter gelatinized, forming a waterproof sediment. Lawin[15] has written more concerning the uses of sodium silicates for this purpose and mentions that the silicate should be one whose soda:silica ratio is not less than 1:3.22. He lists calcium chloride and aluminum sulphate as the two most commonly used salts.

Laws and Page[16] have done some recent work on the use of sodium silicates as soil aggregating and stabilising agents and they make mention of the fact that silicates

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14 Jeglum, op. cit., p. 7.

15 Joseph D. Lawin, "Grouting with Chemicals", Engineering News-Record, 123: 221-22, 1939.

16 W. Derby Laws and J. B. Page, "Silicate of Soda as a Soil Aggregating Agent", The Journal of the American Society of Agronomy, 38: 95-97, 1946.

having higher ratios of silica to soda had a greater aggregating effect and that the calcium and magnesium content of the clay minerals and soils caused an increase in the aggregation by the silicate.[17] Riedel[18] makes similar mention of this fact and adds another point in that the hardness of the solidified soil depends also on the silica and quartz content.

Somewhat allied to the soil stabilization is the work reported by Slobod'yank and Melenivskii[19] who state that the use of sodium silicate as an impregnating agent for diatomic rock improves its properties as a building material inasmuch as a much harder material is obtained. La Fuma[20] also reported that hardening of the silicates can be caused by the addition or presence of hydrolyzable metallic sulfides which decompose in the presence of water

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17 W. Derby Laws and J. B. Page, "Silicate of Soda as a Soil Stabilizing Agent", Highway Research Board, Bulletin Number 1, (Columbus, Ohio: The Ohio State University, 1946)

18 C. Martin Riedel, "Chemical Soil Solidification and Chemical Sealing of Leaking Concrete", Journal of the American Water Works Association, 37: 849-62, 1925.

19 L. Ya. Slobod'yanik and L. A. Melenevskii, "The Effect of Sodium Silicate Solutions on the Physical Properties of Lime-Silica Rock", Stoitel Materialy, 7: 46-49, 1937.

20 Henri Lafuma, "Le Verre Soluble", Chimie et Industrie, 54: 235-43, October, 1945.

to form hydrogen sulfide, the accelerator of the hardening in this case.

III. SODIUM SILICATE IN REFRACTORY MORTARS

Probably the best general discussion on the use of sodium silicates in air-setting refractory mortars is given by Norton[21] who points out that the choice of the plastic bond clay and the soda-silica ratio of the silicate solution determines the properties of the mortar. An analogous field, that of the plastic refractories, is also discussed and a similar difficulty, that of hardening out of contact with air, is cited. Morgan, Peskin, and Kronman[22] have made a study of this hardening and saturated some samples of fuller's earth and plastic fireclays with calcium, magnesium and hydrogen ions after first leaching the materials with hydrochloric acid and washing. The clays were then mixed with sodium silicate solutions and stored in sealed containers. After a period of time, the mixes were noted to have hardened perceptibly. Their explanation of this was that the clays adsorb sodium ions from the

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21 F. H. Norton, Refractories. (New York: McGraw-Hill Book Company, 1942) pp. 373-80.

22 W. R. Morgan, W. L. Peskin, and S. J. Kronman, "Mechanism of the Hardening of Clay-Sodium Silicate Mixtures", Journal of the American Ceramic Society, 23: 170-73 1940.

sodium silicate causing a precipitation of silica gel due to the increase in the silica content of the bonding agent. To overcome this, they suggested that the clays be treated with sodium ions prior to mixing with the sodium silicate, but this, in turn would lower the refractoriness of the mortar.

Jeglum[23] cautions that care must be taken in selecting the dry ingredients of the mortar to eliminate any which contain reactive salts such as those of calcium or magnesium, as they would cause the formation of a rock-like mass in the container.

From this it was noted that there are several factors which must be considered in the study of this problem, namely, the base exchange characteristics of the clay, the amount of soluble heavy metal salts present in the raw material and, from Riedel's work, the amount of free quartz present in the dry materials.

IV. LITERATURE ON BASE EXCHANGE

The first studies of base exchange in soils was made by J. T. Way and H. S. Thompson in 1850 and applications of their work and that of others has been carried on by other soil chemists plus colloidal chemists and ceramic

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23 Jeglum, op. cit., p. 11

research workers who found applications for this phenomenon in their fields. It was not deemed necessary to discuss at great length the history and mechanics of base exchange as considerable has been published on those topics. But it was considered necessary to discuss some of the previous work on the methods of determining exchangeable bases and methods of obtaining hydrogen clay, and subsequently, clays containing other desired cations.

The methods of leaching as described by Graham and Sullivan,[24] Schollenberger and Dreibelbis,[25] Chapman and Kelley,[26] and Kelley and Brown[27] and that of electrofiltration[28] were considered but these methods, used chiefly by the soil chemists, are not too readily applicable to clays.

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24 R. P. Graham and J. D. Sullivan, "Critical Study of Base Exchange Determinations in Clays", Journal of the American Ceramic Society, 21: 176, 1928.

25 C. J. Schollenberger and F. R. Dreibelbis, "Analytical Methods in Base Exchange Investigations on Soils", Soil Science, 30: 161-73, 1930.

26 H. D. Chapman and W. P. Kelley, "The Determination of the Replaceable Bases and the Bases Exchange Capacity of Soils," Soil Science, 30: 391-406, 1930.

27 W. P. Kelley and S. M. Brown, "Replaceable Bases in Soils", California Agricultural Experiment Station, Technical Paper, 15: 1-39, 1927.

28 Amar Nath Puri, "Electrofiltration: A New Method of Removing Exchangeable Bases from Soil Colloids", Soil Science, 30: 413-19, 1930.

which are highly colloidal. Smothers and Herold[29] made a rather careful study of the methods used by previous investigators in order to determine the proper method to study clays and similar materials in their investigation on the flow properties of clay-water mixtures, and their selection of electrodialysis was deemed advisable for this study as well.

Morse and Pierce[30] first observed that the introduction of electrodes into the two chambers of a dialysis cell accelerated the removal of the adsorbed ions from the colloidal material. A few years later, Cameron and Bell[31] used this method in their investigations on the adsorbed ions on soils.

Sante Mattson[32] used a cell of his own design to

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29 W. J. Smothers and P. G. Herold, "A Study of the Flow Properties of Concentrated Clay-Water Mixtures", University of Missouri, School of Mines and Metallurgy Bulletin, Technical Series, (Rolla, Missouri, June 1944), pp. 29-32.

30 Harry W. Morse and George W. Pierce, "Diffusion und Ubersattigung in Gelatine", Zeitschrift für Physikalische Chemie, 45: 600, 1903.

31 Frank K. Cameron and James M. Bell, "Mineral Consituents of the Soil Solution", U. S. Department of Agriculture, Bureau of Soils Bulletin Number 30 (Washington, D. C., 1905), p. 27.

32 Sante Mattson, "Electrodialysis of the Colloidal Soil Material and the Exchangeable Bases", Journal of Agricultural Research, 33: 555, 1926.

determine the exchangeable bases in a soil. His cell consisted of three rubber plates that had been cut in a U-shape and bolted between two hard rubber end plates. He used one hundred grams of dry material in the center cell, but experienced difficulty removing the acid and basic materials from the surfaces of his outer chambers in order to make quantitative determinations. Another difficulty experienced in his work was the fact that no provisions had been made for stirring the soil in the center chamber and, as a result, the soil settled out during dialysis, making any quantitative conclusions erroneous. A similar cell was made by Bradfield[33] by cutting a storage battery into three sections, but like Mattson's cell, the removal of the acids and bases from the outer compartment was difficult.

Smothers[34] concluded that a glass cell would be more readily cleaned and used Pyrex glass tubing, cut to the desired size and sealed with a water resistant wax. Distilled water was admitted at a predetermined rate into each of the two electrode chambers and the overflow was retained for testing. A similarly designed cell was used by Norton

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33 Richard Bradfield, "An Inexpensive Cell for the Purification of Colloids by Electrodialysis", Industrial and Engineering Chemistry, 20: 79-80, 1928.

34 Smothers and Herold, op. cit., pp. 29-33.

and Johnson[35] except that the outer two compartments were made of porcelain and the center compartment was constructed of a plastic. A recent work by Tha Hla[36] in studying artificial rock weathering, utilized an electrodialysis cell of plastic construction and agitated the clay suspension by bubbling carbon dioxide through the bottom of the central compartment. Norton and Johnson utilized a reciprocating rubber paddle for this purpose.

Most of the investigators mentioned above have drawn the same conclusion from their work on electrodialysis, that all of the adsorbed ions are not removed from the colloid in the center compartment. There are, however, advantages to be gained by the use of this method over that of leaching, the greatest being that insoluble salts present in the clay would not probably be removed by electrodialysis, whereas with acid leaching, many of them would probably be dissolved and be analyzed with the leach liquor.

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35 A. L. Johnson and F. H. Norton, "Fundamental Study of Clay; Preparation of a Purified Kaolinite Suspension, I", Journal of the American Ceramic Society, 24: 64-69, 194.

36 Tha Hla, "Electrodialysis of Mineral Silicates: An Experimental Study of Rock Weathering", Mineralogical Magazine, 27: 137-45, 1945.

CHAPTER III

FORMULAE AND MATERIALS

I. FORMULAE

Inasmuch as this work was done under an industrial fellowship, it was not deemed proper to disclose the exact formulae used in the preparation of the mortars for test purposes. For this reason, the compositions listed in Table I show only the per cent of dry and wet materials, with the letter "x" in the appropriate column indicating the presence of the material and the letter "o" indicating its absence from that particular mortar.

TABLE I

COMPOSITION OF MORTARS STUDIED

Material	Mortar "A"	Mortar "B"	Mortar "C"
Dry, Including	73.5%	73.5%	73%
Clay	x	x	x
Diaspore	x	x	o
Kyanite	o	x	x
Silica Dust	x	o	o
Bentonite	x	x	x
Wet, Including	26.5	26.5	27
Sodium Silicate	x	x	x
Water	x	x	x

In some, the bentonite was left out of the batch composition and these mortars will be referred to as Mortar "Ax", Mortar "Bx" and Mortar "Cx".

II. MATERIALS USED

Clay. Two different clays were used in this study inasmuch as Smith[37] pointed out that, with any given formula, each of the two clays caused different gelling characteristics in the mortar. A description of each clay follows.

1. Weatherall Plastic. This is one of the Upper Member clays of the Cheltenham formation and is mined in the Weatherall pit, NW¼ SE¼, Sec. 29, T. 48 N., R. 9 W., Callaway County, Missouri. McQueen[38] describes the lithologic character of the clays of this formation as follows:

> "The Clay of the upper member is uniform in general make up. It is nearly always a bluish gray color. It is fine-grained, but lacks the smooth, even texture of the lower clays. It is also not as hard, and the slickensided surfaces of the lower clays are almost lacking, and where present are not as highly developed. . .
>
> "Two features, however, serve to distinguish the

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37 C. A. Smith, Chief Engineer, Mexico Refractories Company, Mexico, Missouri. Personal correspondence with the author.

38 H. S. McQueen, Geology of the Fire Clay Districts of East Central Missouri, (Rolla, Missouri, Missouri Geological Survey, Volume 28, Second Series, 1943), pp. 62-63.

> clay. First the clay upon weathering slacks or breaks down into extremely fine angular particles, and second, with prolonged surface weathering it becomes a gray, sticky, highly plastic mass. Neither of the foregoing properties is common to the other members of the Cheltenham."

The chemical composition of this clay appears in Table II. On the chemical composition, McQueen reports that "This clay has the highest ratio of silia to alumina of any of the clays of the Cheltenham formation. The silica content approaches or exceeds 55 percent and the alumina is less than 30 percent. Fluxing impurities are higher and iron, chiefly as pryite, is present."[39] It will be noted that the Weatherall clay used generally agreed with the foregoing statement.

TABLE II

CHEMICAL ANALYSIS OF WEATHERALL CLAY

SiO_2	57.64%
Al_2O_3	26.70
Fe_2O_3	1.84
CaO	.75
MgO	.68
TiO_2	.83

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39 McQueen, op. cit., p. 64.

TABLE II (continued)

CHEMICAL ANALYSIS OF WEATHERALL CLAY

Na_2O & K_2O	1.64
Ignition loss	9.96
Total	100.04

Petrographic examination of the Weatherall clay sample used showed principally kaolinite, with some pyrite and calcite crystals and many small quartz crystals. One interesting observation was the presence of a glassy-like amorphous material with high relief, but low index of refraction. The indices ranged from 1.41 to 1.45 and the material was identified as opal. There was not a great abundance of this material present, but sufficient to make note of it. McQueen's description of a sample of clay taken from this same pit was that it "contains. . .kaolinite. . .and also much iron stained opaque areas of clay. The crystals of pyrite are very few in this sample . . . There are many fine grains of quartz scattered through the clay as well as carbon and a very few minor mineral."[39]

2. Stoltz Plastic. This is one of the clays of the Loutre formation and is mined on the Stoltz farm, NW¼ sec. 34, T. 48 N., R. 9 W., Callaway County, Missouri. The

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39 McQueen, op. cit., pp. 242-43.

Loutre clays, according to McQueen,[40] were deposited in a succession of strata on the surface of the Cheltenham clay. It has been generally found in every pit in the East-Central Missouri area, and is usually avoided in mining operations. Some of the clays, such as the clay from the Stolts pit, are used as they seem to have undergone alterations with the leaching of soluble salts. McQueen describes the weathering of the formation and states that during the period of subsequent erosion of the upper member, "the underclay. . . was purified, locally at least, to the extent that it is used for refractory cements and mortars. Physically, it was changed from a soft plastic to a fairly hard, semi-plastic, and perhaps even a semi-flint clay, as is the case of the clay as now developed in the Mexico Refractories pit . . ."[41]

The chemical analysis of the Stolts clay used in this work appears in Table III.

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40 McQueen, op. cit., pp. 71-73.

41 McQueen, op. cit., p. 78.

TABLE III

CHEMICAL ANALYSIS OF STOLTZ CLAY

SiO_2	52.38%
Al_2O_3	31.25
Fe_2O_3	1.54
CaO	.80
MgO	.53
TiO_2	.89
Na_2O & K_2O	1.46
Ignition loss	11.24

Petrographic analysis showed the presence of kaolinite and silica, principally, with some pyrite and calcite. The results of the microscopic analysis given by McQueen showed the presence of halloysite,[42] but none was observed in the samples studied in this work. It should be noted here that the Stolz clay did not have as many quartz crystals in evidence as did the Weatherall clay.

Diaspore. The diaspore clay used in this study is the high alumina clay found in the sink-hole deposits of east-central Missouri. Prior to its use in the manufacture of refractory mortars, the diaspore clay is calcined at a temperature around 1000 degrees centigrade. The calcined clay is then pulverized, so that all of the material passes

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42 McQueen, op. cit., p. 241.

through a 100 mesh sieve.

Kyanite. The kyanite used in this study was 100 mesh raw North Carolina kyanite.

Silica Dust. This material is very fine (300 mesh) silica powder obtained from one of the plants processing St. Peter sandstone in the St. Louis area.

Bentonite. Wyoming Bentonite (trade name--Volclay) was used.

Sodium Silicate. Inasmuch as the properties and characteristics of the various brands of sodium silicate had been discussed, it was decided to use just one type of sodium silicate in this study. The brand used was Number 26, manufactured by the Grasselli Chemical Company. This material analyzes 13 per cent Na_2O and 29 per cent SiO_2, so that the soda-silica ratio of this silicate is about 1:2.23. The samples obtained varied, as shown in Table IV, but these variations are slight enough to be overlooked.

TABLE IV

ANALYSES OF SODIUM SILICATES

Sample Number	Na_2O	SiO_2	Ratio
1	12.8%	29.2%	1:2.27
2	12.1%	28.7	1:2.36
3	13.9	29.6	1:2.12

Water. Ordinary tap water was used in all work except where noted.

CHAPTER IV

EXPERIMENTAL PROCEDURES

I. TESTING THE WORKABILITY OF MORTARS

1. Equipment. No standard test has been required by the American Society for Testing Materials for determining the workability or consistency of air-setting refractory mortars. They have, however, given a specification of the quality of the material.

> "3. The mortar shall be sufficiently free from grit and of such quality and plasticity that it will spread satisfactorily with a trowel, either as it comes from the container or after a moderate amount of tempering with water. . .At any time within a 6-month period after purchase, the mortar in a newly opened container shall not have stiffened or hardened to such an extent as to prevent its easy removal and mixing."[43]

A test was needed, then, in order to obtain a relative measure of the gelation in place of using the terms "good", "fair" and "poor", or some similar description that is commonplace to various manufacturers. The most satisfactory test for measuring the flow of a newly mixed mortar was that used as a standard test by the Amer-

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43 "Tentative Specifications for Air-Setting Refractory Mortars (Wet Type) for Boiler and Incinerator Services. A.S.T.M. Designation: C 178-44T", 1944 Book of A. S. T. M. Standards, Part II Nonmetallic Materials--Constructional, (Philadelphia, Pa., American Society for Testing Materials, 1944), p. 1291.

ican Society for Testing Materials for the flow of portland-cement using the flow table.[44] Instead of the specified thirty inch diameter table with a ten inch diameter cone, a modified table was used. The diameter of this flow table was twelve inches and the inside diameter of the base of the truncated cone mold was four inches.

The specifications required that the concrete be rodded with twenty-five strokes of a round rod. This procedure was satisfactory for a freshly prepared mortar, but was not deemed satisfactory for testing gelled mortars, as the rodding would tend to break up the gel structure formed. After assuring an even distribution of the mortar in the mold, the excess was removed and the mold lifted off the table, leaving the mortar in place. The table was then raised and dropped one-half inch fifteen times in about fifteen seconds. The diameter of the spread was then measured, taking the average of six symmetrically distributed caliper measurements, read to the nearest quarter inch.

The flow of the mortar was then recorded as the percentage increase in the diameter of the spread mortar over the base diameter of the molded mortar. The following

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44 "Standard Method of Slump Test for Consistency of Portland-Cement Concrete. A.S.T.M. Designation C 143-39", 1944 Book of A.S.T.M. Standards, Part II, Nonmetallic Materials--Constructional, (Philadelphia, Pa., American Society for Testing Materials, 1944), pp. 476-77.

formula was used to make this calculation:

$$\text{Per cent Flow} = \frac{\text{Spread Diameter} - 4 \text{ inches}}{4} \times 100$$

An additional modification could possibly be made to this test to make it readily applicable to this type work, that being the use of a container the shape of which conformed to the specifications of the mold. In this way the hardened mortar could be placed on the table without breaking the gel structure and still assure the operator that the mortar was evenly distributed before removing the mold. This would, however, have entailed such expense that it was not deemed advisable for this study.

Instead, a modification was made to the test designed for the determination of the normal consistency of gypsum plaster.[45] A 5/8 inch aluminum rod 8½ inches long, guided by a metal collar, was made to penetrate the mortar by adding weights to a three inch pan fastened to the top of the rod. The rod itself was calibrated in half-centimeter intervals and a section of the guide was cut out to

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45 "Standard Methods of Testing Gypsum and Gypsum Products. A.S.T.M. Designation: C 26 - 42", 1944 Book of A.S.T.M. Standards, Part II, Nonmetallic Materials--Constructional, (Philadelphia, Pa., American Society for Testing Materials, 1944), pp. 149-50.

permit the reading of this scale. (See Figure 1.) The rod was held in a vertical position by means of a clamp on the collar, the clamp being fastened to a ring-stand. The mortars were mixed and placed in glass jars which were 2½ inches in diameter and four inches high. Sufficient weight was added to the modified Vicat apparatus to cause a penetration of 50 mm, plus or minus 10%.

The weight required to make the penetration was recorded in all cases. The minimum weight usable, the weight of the rod and the pan, was 180 grams. This weight was too great for a 50 mm penetration of some mortars, so an extrapolation had to be made in these cases. These will be marked with an asterisk (*) in the data and charts.

Inasmuch as most mortars used had different consistencies after mixing, it was decided to calculate the percentage increase in the weight required to make a penetration after storage. In this manner a relative comparison could be made among a series of different mortars. This will be reported in "percent gelation" and was calculated from the following formula:

$$\text{Percent Gelation} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 = weight required for 50 mm. penetration after mixing

W_2 = weight required for 50 mm. penetration after storage

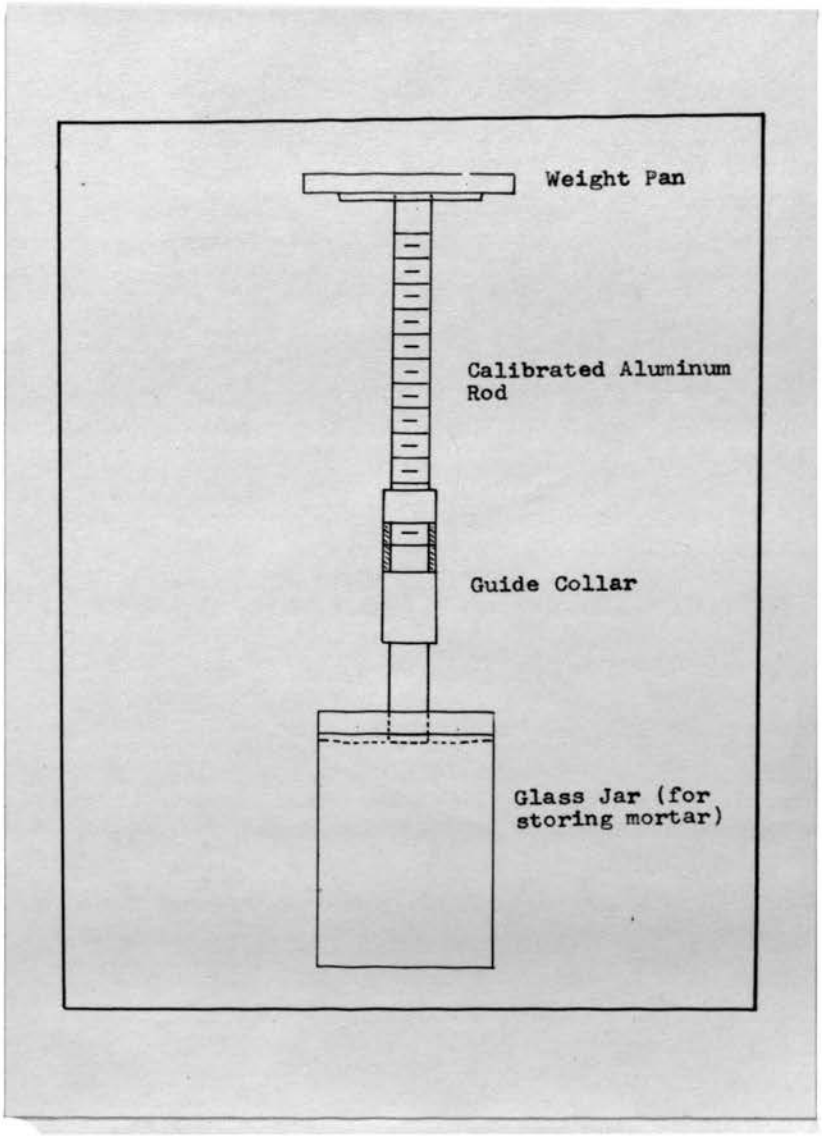

Figure 1.

Modified Vicat Apparatus for Measuring Mortar Workability.

It should be pointed out here that this figure was not intended to indicate the percentage of the mass which was a gel, but rather the increase in the so-called "hardening". In a way, it might be considered a measure of the viscosity of the mixture.

2. Storage. Several accelerated tests have been suggested to decrease the time between the preparation and the measuring of the gelled mortar. Morgan, Peskin and Kronman[46] placed the mortars or mixtures in sealed containers and kept them at a temperature of 60° centigrade for three days. Some refractories manufacturers use an accelerated test method in their laboratory by placing the mortar in a sealed container and subjecting it to a temperature of 168° Fahrenheit (76° C.) for sixteen hours. This latter method was used in some cases, but generally the mortars were placed in sealed containers and stored at room temperatures for a period of from three to four weeks. In all cases, the water content of the mortar was measured immediately after mixing and again after storage. The water content after storage was found to be within 2% of the original.

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46 Morgan, Peskin and Kronman, op. cit., p. 171.

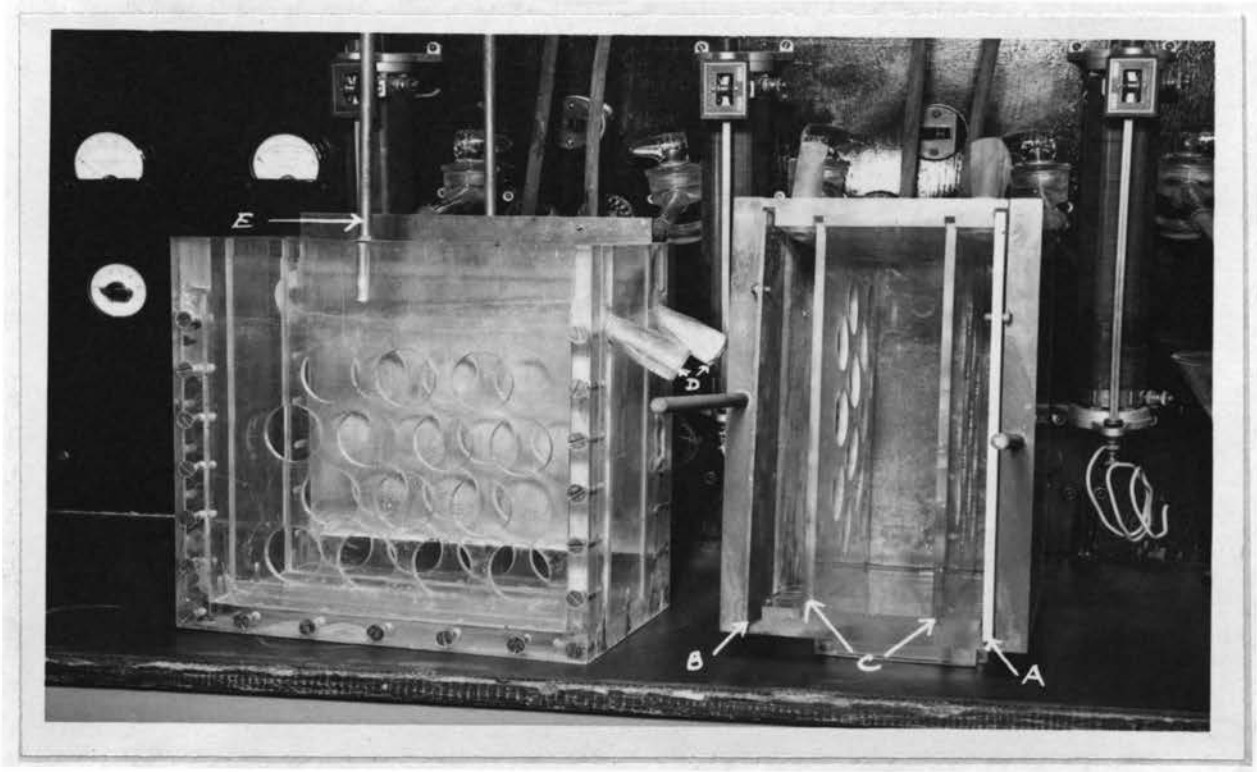

Figure 2

Large Electrodialysis Cells, showing (a) the aluminum anode, (b) copper cathode, (c) compartment partitions, (d) overflow plugs, and (e) the supports for the air motors.

The cells were constructed with slots in the front and back of each side so that the electrodes (a and b) would always be the same distance apart.

The compartment partitions (c) were made of 3/8 inch Plexiglass and each was drilled with fourteen 1½ inch holes. The first method of installing the membrane paper consisted of fastening the animal parchment to the inside of the partitions with a collodian base, plastic cement. This method, although making the center compartment completely separate from the two outer compartments, was not too successful due to the fact that the membranes separated from the partitions as the cement shrunk. This permitted the clay to migrate into the electrode compartments making further removal of ions impossible.

A second, more successful method was to fold the parchment paper so that a rectangular bag was formed that just fit into the center compartment. The folds were so arranged that all of the open ends of the bag were above the height of the overflows. The clay-water mixture was placed in the membrane bag and, although the two electrodes were not completely separated, the electrodialysis proceeded properly.

Two hundred grams of clay that had been blunged in distilled water for 24 hours were used in the large cells. The center compartments held 4.5 liters and the electrode

compartments held two liters of distilled water each. Distilled water was circulated through the electrode chambers at the rate of 20 ml. per minute. If desired, the effluents could be retained in 2l liter Pyrex carboys. The variable resistors made possible the application of from 90 to 220 volts d. c. potential across each cell. If lower voltages were desired, a full wave rectifier, gas tube regulated power supply was used as the power source.

The clay was kept in suspension by two glass stirrers at either end of the center compartment. The stirrers were operated by small compressed air motors. Very little clay was found to cling to the anode side of the membrane and the material was kept in suspension, even towards the completion of the procedure. The dialysis bench used is shown in Figure 3.

Norton and Johnson[49] pointed out that the ions are removed in definite steps and that the pH of the center chamber was an indication of the type of ion removed. A study of the charts in their work and similar work done in this department, seemed to indicate that the current flow was also a measure of the amount and types of ions being removed. For this reason, readings were taken of the voltage, current, temperature and, in many cases, pH of the

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49 Norton and Johnson, op. cit., pp. 65-66.

Figure 3.

Electrodialysis Bench, showing (a) low voltage power supply, (b) voltmeter, (c) milliammeter selector switch, (f) four point recording potentiometer, (g) variable resistor, (h) power switch for the individual cell, (i) distilled water valves, (j) air pressure gauge, (k) air stirrers, (l) compressed air valves, (m) distilled water supply, (n) electrodialysis cells.

center compartment. The installation shown in Figure 2 was so wired that readings could be made on four cells operating simultaneously. The recording potentiometer was so adapted as to act as a four point recorder. This potentiometer measured the voltage drop across a small resistance in each circuit. This measured relatively, in effect, the current flowing through the circuit. The wiring diagram of the entire installation is shown in Figure 4.

Low voltages were used at the beginning of the electrodialysis so that the ions would be removed more slowly and the temperature of the clay-water mixture would be kept lower. As the process progressed, the potential was increased in steps until the maximum voltage, 220 volts d. c., was reached. The electrodialysis was considered complete when no change occurred in the pH or the current.

The chief advantage of the large cells was that fairly large quantities of hydrogen clay could be prepared. After the dialysis was completed, the hydrogen clay was stored in sealed, paraffine-lined cans to prevent contamination.

In the early part of this work, graphite anodes were used in the large cells. It was found, however, that after about 30 hours, the cathode effluents began to turn a light brown--eventually becoming a very dark brown. This had been

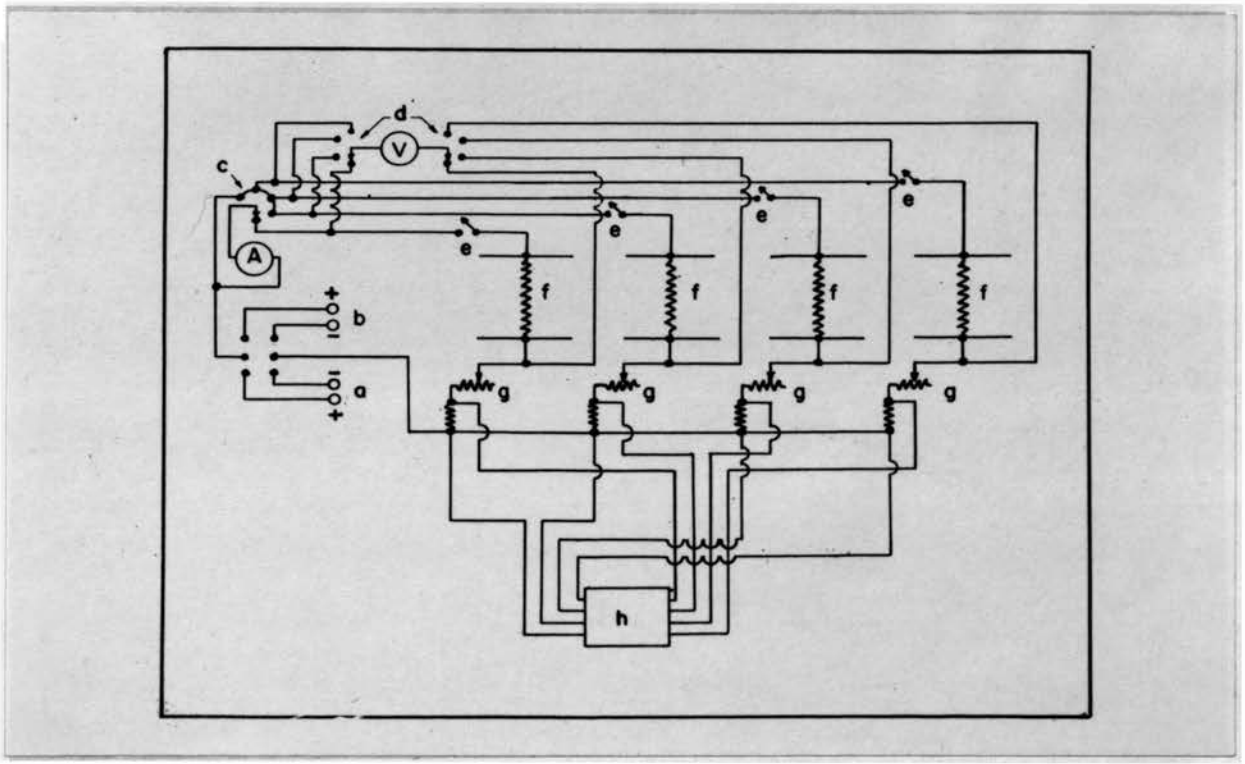

Figure 4.

Wiring Diagram of the Electrodialysis Bench, showing (a) D. C. rectifier (low voltage power supply), (b) 220 volt D. C. power line, (c) 5 pole, short circuit type, ammeter switch, (d) 4 pole, 2 section, voltmeter switch, (e) individual panel switches, (f) electrodialysis cells, (g) variable resistors, and (h) four point recording potentiometer.

reported previously by Smothers and Herold[50] and was thought to be due to the high iron content of the clays being studied. It was not believed, however, that the iron content of the clays under consideration here would account for all of this discoloring, so an aluminum anode was installed in one of the cells. A check was made using two cells, each filled with distilled water, one using the graphite anode and the other an aluminum anode. The same voltage (200 v. d. c.) and resistance was utilized in both cells and current and temperature readings were taken periodically on both cells. No distilled water was run through these cells during this test and no membrane paper was used. Figure 5 shows a comparison of the current flowing in the two cells.

The discoloration in the cell using the graphite anode became evident after 32 hours, and was believed to be due to the dissociation of the bonding material in the electrode. This phenomena did not seem to be so pronounced when the electrodes were new, but got progressively worse with continued use. A white, gelatinous material began to appear after 24 hours in the cell using the aluminum anode. This material migrated rather slowly towards the cathode, but was not present in very large quan-

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50 Smother and Herold, op. cit., p. 52.

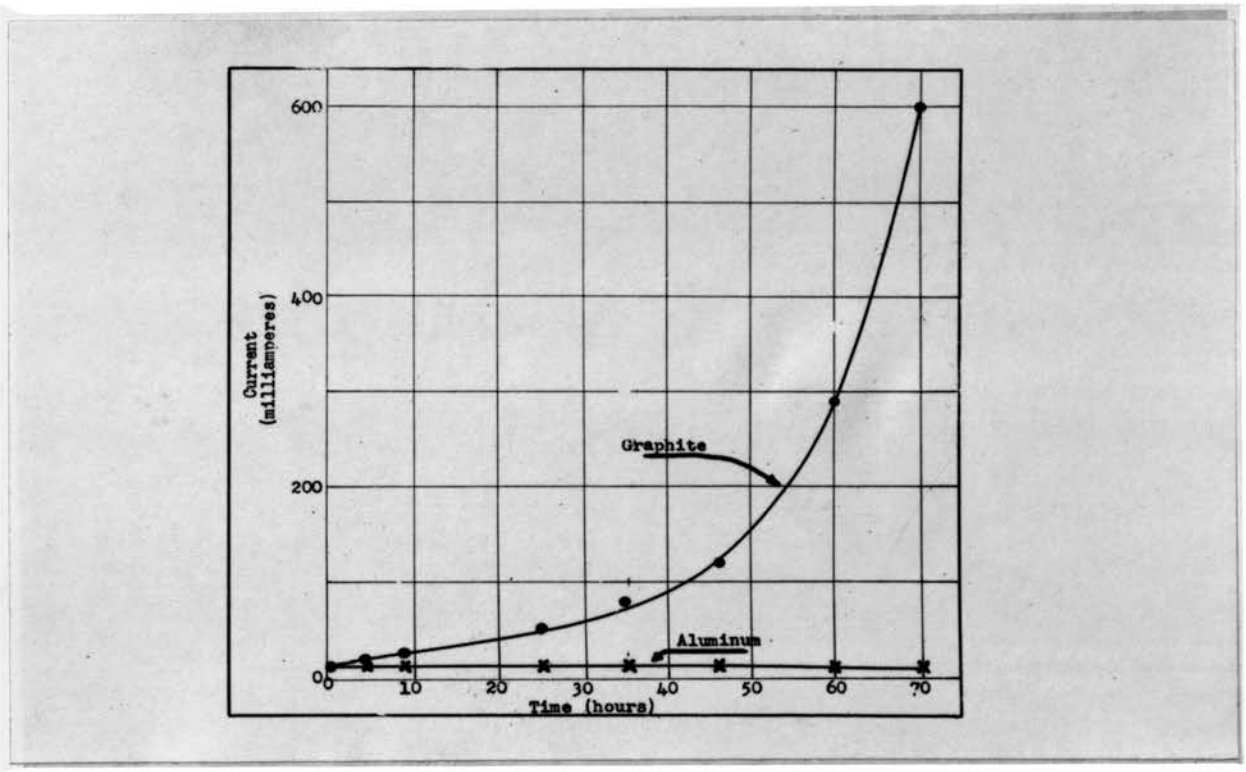

Figure 5.

Current Flow Through Distilled Water using an Aluminum Anode and a Graphite Anode.

tities. A sample of this material was dried and an x-ray diffration pattern from it identified it as B $Al(OH)_3$, or bayerite. Upon removal of the electrode after the test, the inside face appeared to be "etched", indicating that the aluminum had been attacked around the grain boundaries. In all further tests, aluminum alloy 528 was used as the anode material.

The smaller cells shown in Figure 6 were built in order to use smaller quantities of clay and water and to make a more accurate check on the contents of the two effluents. These cells were also constructed of Plexiglass the center compartments consisting of a two inch length of 3 inch tubing. A ½ inch hole was bored in the center of one side of the tubing so that the clay and water could be admitted to the center compartment. Copper was again used as the cathode electrode, but platinum was used as the anode. Membrane paper was placed on either side of the center tube and the three pieces held together by four bolts. In this way, the cell was watertight and no liquid could pass around the membrane, as was possible with the parchment bags used in the large cells.

These cells were installed on the dialysis bench using the same wiring plan as before. In an attempt to study the removal of all ions, both adsorbed and those of the soluble salts present, the dry clay was added to the

center cell just prior to the application of the potential. The clay was kept in suspension by means of a propellor type of mixer made from Plexiglass and driven by one of the air stirrers. The center member of Figure 6 shows how this stirrer was placed in the center compartment. The cathode effluents were retained in the large Pyrex carboys for further analysis.

III. BASE EXCHANGE CAPACITY

The method used by Meyer[51] was employed in determining the base exchange capacity of the clays. Stock solutions were prepared of 0.1 N sodium chloride, containing 0.0, 0.05, 0.1, 0.2, and 0.3 milliequivalents of added sodium hydroxide and 0.05, 0.1, and 0.2 milliequivalents of hydrochloric acid, respectively, per 25 ml. of solution.

The pH of each of the stock solutions thus made was determined using a Beckman Laboratory Model pH Meter and these values plotted against the concentration of the acid or base in the neutral salt solutions. Then one gram of hydrogen clay was added to each 25 ml. of the stock solutions and allowed to stand for 96 hours with periodic shaking (about three times daily). The pH of these clay-electroloyte-water mixtures was then determined and the

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51 W. W. Meyer, "Clay Colloids and Related Properties" U.S. Bureau of Standards, Journal ofResearch, 13: 251, 1934.

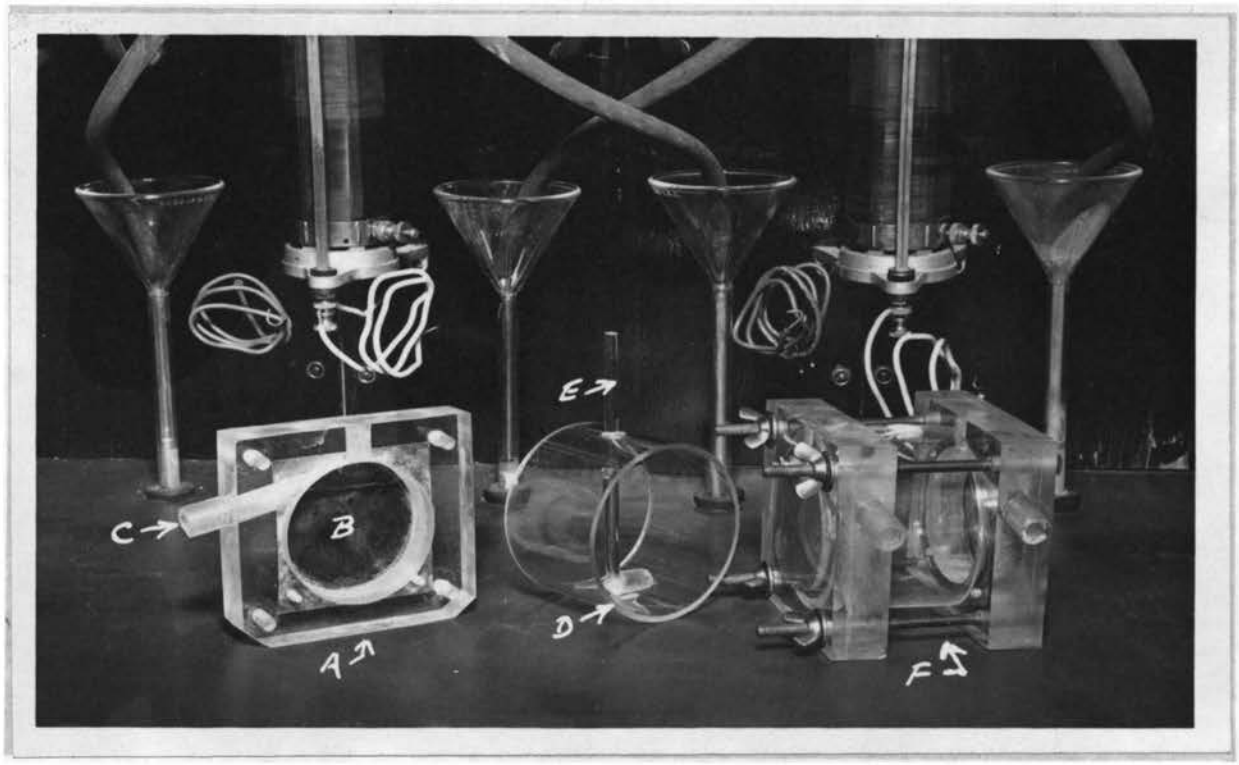

Figure 6.

Small Electrodialysis Cells, showing (a) cathode compartment, (b) copper cathode, (c) overflow plug, (d) center compartment, (e) plastic stirrer, and (f) the assembled cell.

values obtained plotted against the electrolyte concentration. At any given pH, the horizontal distance between the two curves so obtained represented the exchange capacity of the clay in equilibrium with the neutral salt (sodium chloride) for chlorine or for sodium. The base exchange capacities given in this paper have been taken for the various materials at a pH of 7.0.

IV. DIFFERENTIAL THERMAL ANALYSIS

The use of differential thermal analysis to identify mineral constituents of clays has been used to varying degrees of success by a number of investigators. Norton[52] describes qualitative and quantitative methods of determining the mineral constituents and Grim has written several papers[53] on the subject. Keller recently published a

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52 F. H. Norton, "Critical Study of the Differential Thermal Method for the Identification of Clay Minerals", Journal of the American Ceramic Society, 22: 54-63, 1939.

53 (a) Ralph E. Grim and Richard Rowland, "Differential Thermal Analysis of Clay Minerals and other Hydrous Materials", Report of Investigations Number 84, (Urbana, Illinois; Illinois Geological Survey, 1942).

(b) Ralph E. Grim and R. A. Rowland, "Differential Analysis of Clays and Shales, a Control and Prospecting Method", Report of Investigations Number 96, (Urbana, Illinois; Illinois Geological Survey, 1944).

(c) Ralph E. Grim, "Differential Thermal Curves of Prepared Mixtures of Clay Minerals", Report of Investigations Number 134, (Urbana, Illinois; Illinois Geological Survey, 1948).

paper[54] giving the results of the work done on Missouri fireclays. It was thought that, if mineral constitution of the clay played any part in the problem being studied, this analytical tool would be of great assistance in determining the composition of the clay.

The equipment designed and described by Herold and Planje[55] was used in this work. The sintered alumina sample holder as described was used, except that the cup differential thermocouple was omitted. In its place, a differential thermocouple made of 87% platinum-13% rhodium and platinum was used.

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54 W. D. Keller and J. F. Wescott, "Differential Thermal Analysis of some Missouri Fireclays", Journal of the American Ceramic Society, 31: 100-05, 1948.

55 Paul G. Herold and T. J. Planje, "Modified Differential Thermal Analysis", Journal of the American Ceramic Society, 31: 20-22, 1948.

CHAPTER V.

EFFECT OF DIFFERENT MIXES AND MATERIALS

The difference in workability between the three basic mortars was first determined. Sample batches of each of the mortars "A", "B", and "C" were made using Weatherall clay and their workability measured immediately after mixing. The mortars were then placed in sealed cans and stored at room temperature for four weeks, and the workability again determined. The differences are shown in Figure 7. These tests indicated a definite difference between mortar "A" and the other two. There was some difference in the gelation of "B" and "C", but it was not as pronounced as the other.

The next tests performed were a comparison of the two clays using a given mixture, which in this case was mortar "B". A number of samples of each mortar was made so that the rate of gelation could be studied. The results are shown in Figure 8.

It was interesting to note that both clays required the same number of grams to obtain a similar depth of penetration. However, the mortar made using the Stolts clay was more fluid immediately after mixing than that using the Weatherall clay, so that the <u>percent gelation</u> was greater for the Stoltz. In running these tests, it was found that

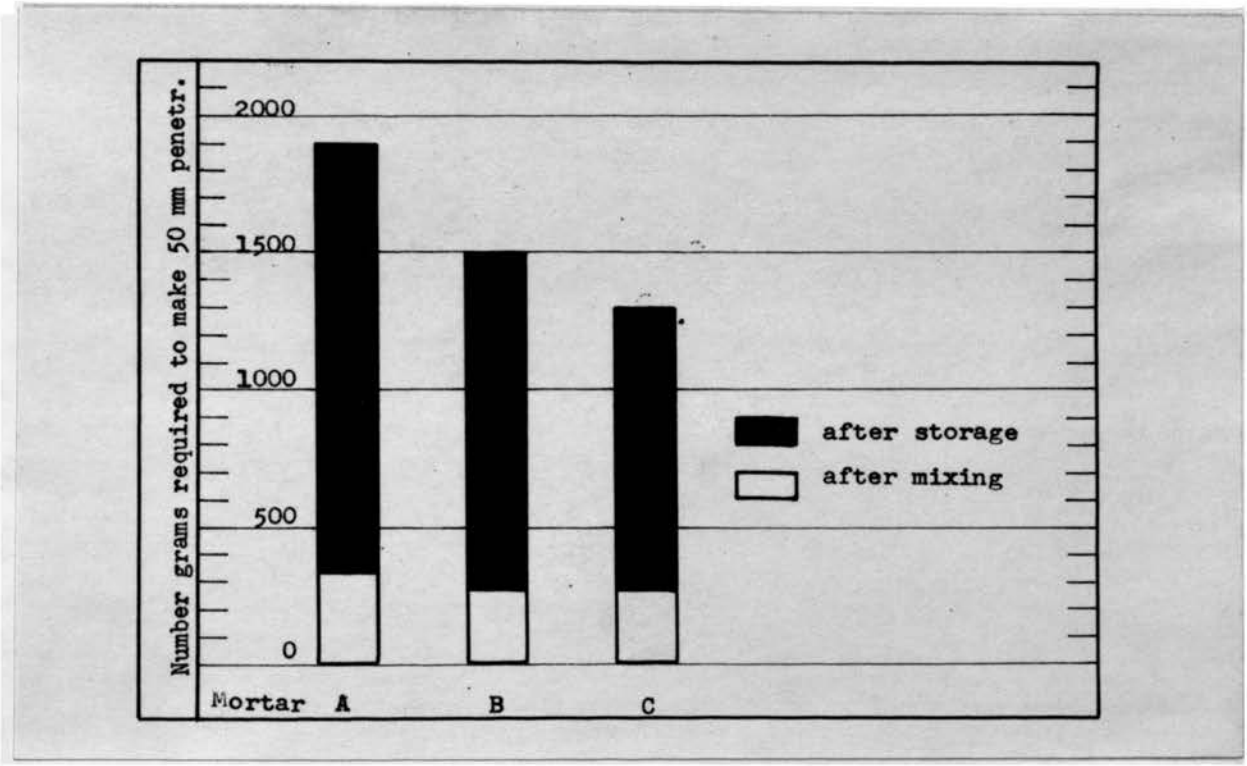

Figure 7.

Workability of Mortars "A", "B", and "C".

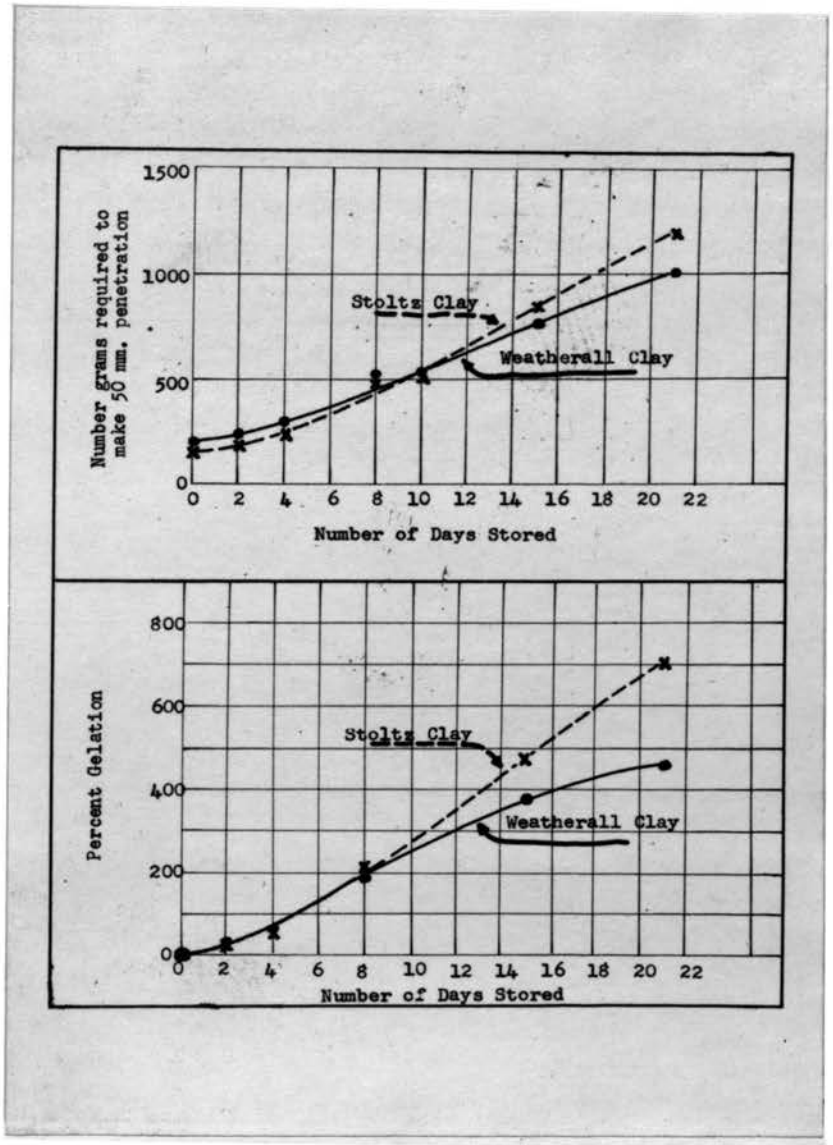

Figure 8.

Rate of Gelling of Morter "B" using Weatherall Clay and Stoltz Clay.

any mortar requiring more than 700 grams to make a 50 mm. (± 5 mm.) penetration was not satisfactory.

The chief purpose of the bentonite in the mix was to keep the mortar in suspension during storage. Several tests were run to determine whether or not any detrimental effects were due to this material being present. The results of these are shown in Figure 9.

Increasing the bentonite definitely seemed to cause an increase in the gelling properties of the mortar. The mortar without any bentonite addition seemed to be as well dispersed as those with the additions. It was deemed advisable, therefore to check this further on the additional tests to be made with admixtures.

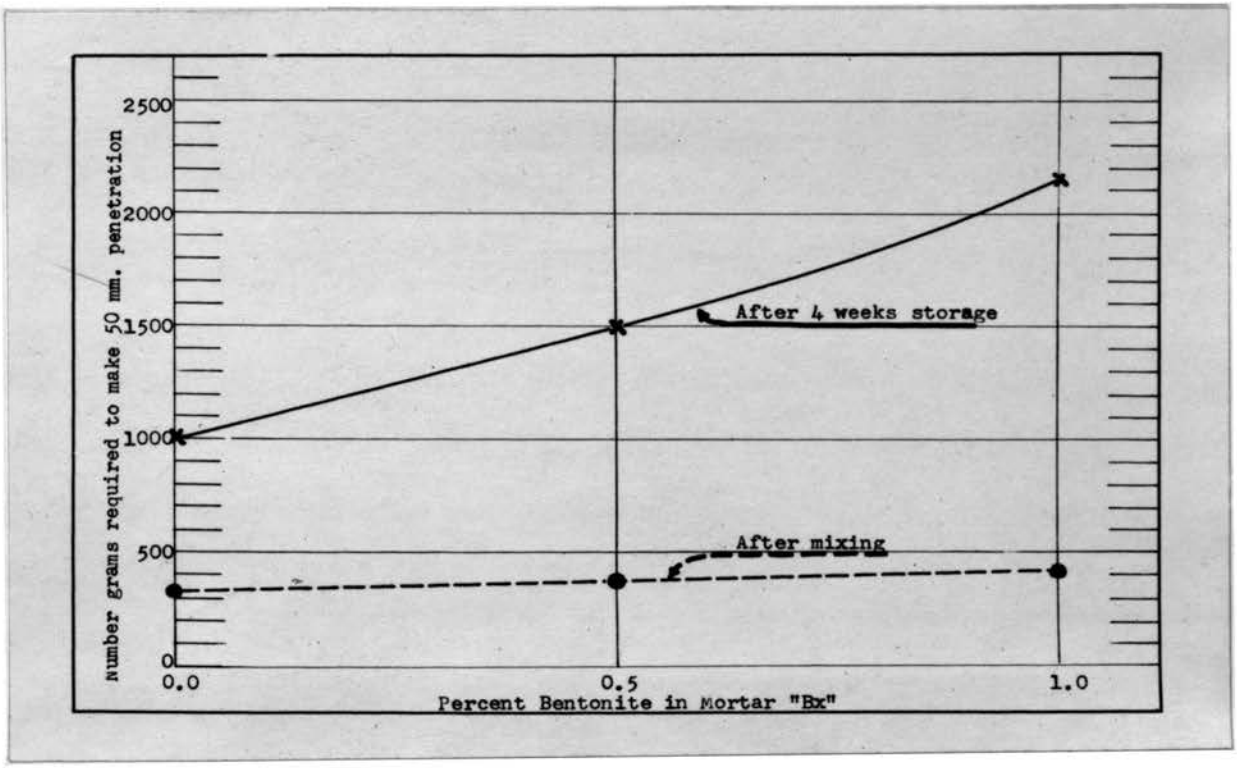

Figure 9.

Effect of the Addition of Bentonite to Mortar "Bx" on the Workability of the Mortar.

CHAPTER VI.

EFFECT OF ADMIXTURES

The detrimental effect of gelation has been overcome in some manufacturers laboratories by adding certain materials to the mortar. These admixtures were numerous and heterogeneous. A study was made of the results of some of these admixtures in this investigation.

Inasmuch as the gelation was felt to be due to a reaction of some type between the dry portion of the mix and the sodium silicate, it was thought that the addition of a protective colloid would have a desired effect. A number of materials were chosen, chiefly because of their known protective action.

A number of tests were run to determine the proper amounts of these materials to add. It was found that no more than 0.5 per cent of these admixtures could be used satisfactorily. If more was used, additional water was needed to keep the proper consistency and caused the total water content of the mortar to be too high. In some cases, less of the materials were added, depending upon the properties of the material.

Some of these were found to give the mortar a poor dry strength, so modulus of rupture tests were made accord-

ing to the ASTM Tentative Specification C 178 - 44 T.[56] Although the requirements of these specifications called for a strength of not less than 200 pounds per square inch (psi), it was desired in this work to have a strength of at least 700 psi.

In preparing these mixtures, mortars "B" and "Bx" were used. The addition was first dissolved in the water, the dry materials thoroughly mixed, and the solution added. After further mixing, the sodium silicate was added. Weatherall clay was used in all tests. The results obtained are given in Figure 10.

Tests were also made on the effect of neutral salts added to the mortar. Again mortars "B" and "Bx" were used and the results are shown in Figure 11.

It should be noted again that a considerable difference in workability is obtained when the bentonite is left out of a mixture. In no case did any of the mortars prepared settle out during storage.

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56 "1944 Book of A.S.T.M. Standards, Part II, Non-Metallic Materials--Constructional", (Philadelphia, The American Society for Testing Materials, 1944), p. 1291.

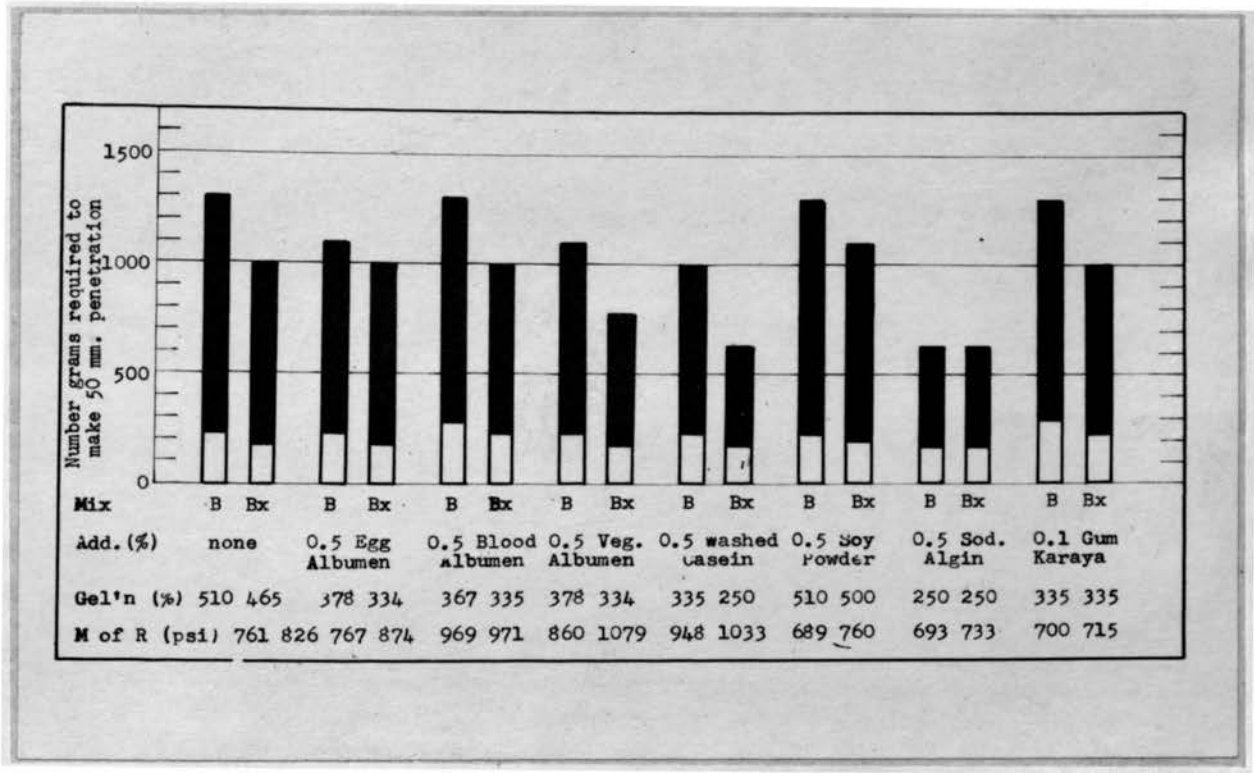

Figure 10.

Workability and Strength of Mortars "B" and "Bx" with the Addition of Protective Colloids.

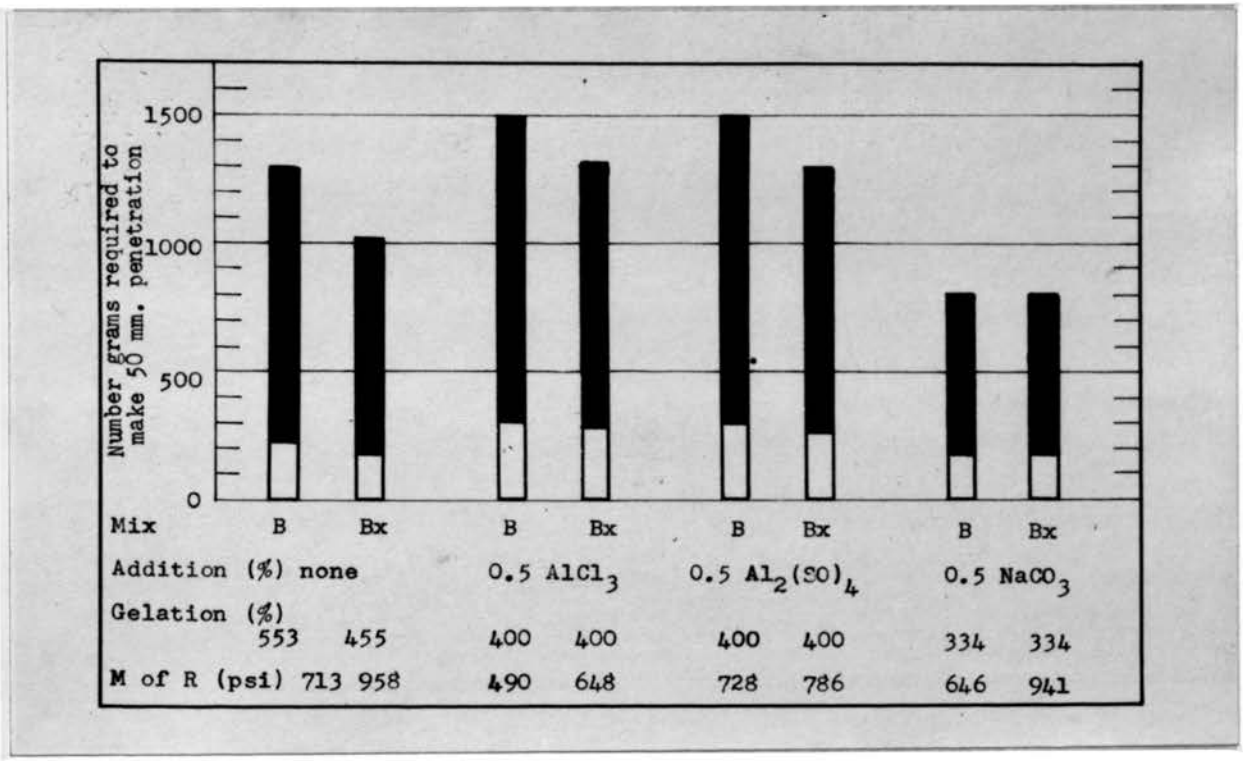

Figure 11.

Workability and Strength of Mortars "B" and "Bx" with the Addition of Neutral Salts

CHAPTER VII.

EFFECT OF ADSORBED IONS

In order to determine the effect of the adsorbed ions on the workability, it was necessary to first remove all of the adsorbed ions from the raw clays. This was accomplished by electrodialysis. A graph showing the current flow versus the time (volt-hours/centimeter) of dialysis for the two clays is shown in Figure 12.

If, as previously mentioned, the areas under the peaks of these curves are a quantitative measure of the ions being removed, then it would seem that the Stolts clay had more ions removed than the Weatherall clay. It would also follow that the Stolts clay had the higher base exchange capacity.

The base exchange capacities were determined for all dry materials used in the mortars, with the exception of the bentonite. The pH curves for determining these exchange capacities are shown in Figures 13 through 17 inclusive and the base exchange capacities observed at a pH of 7.0 are given in Table VI.

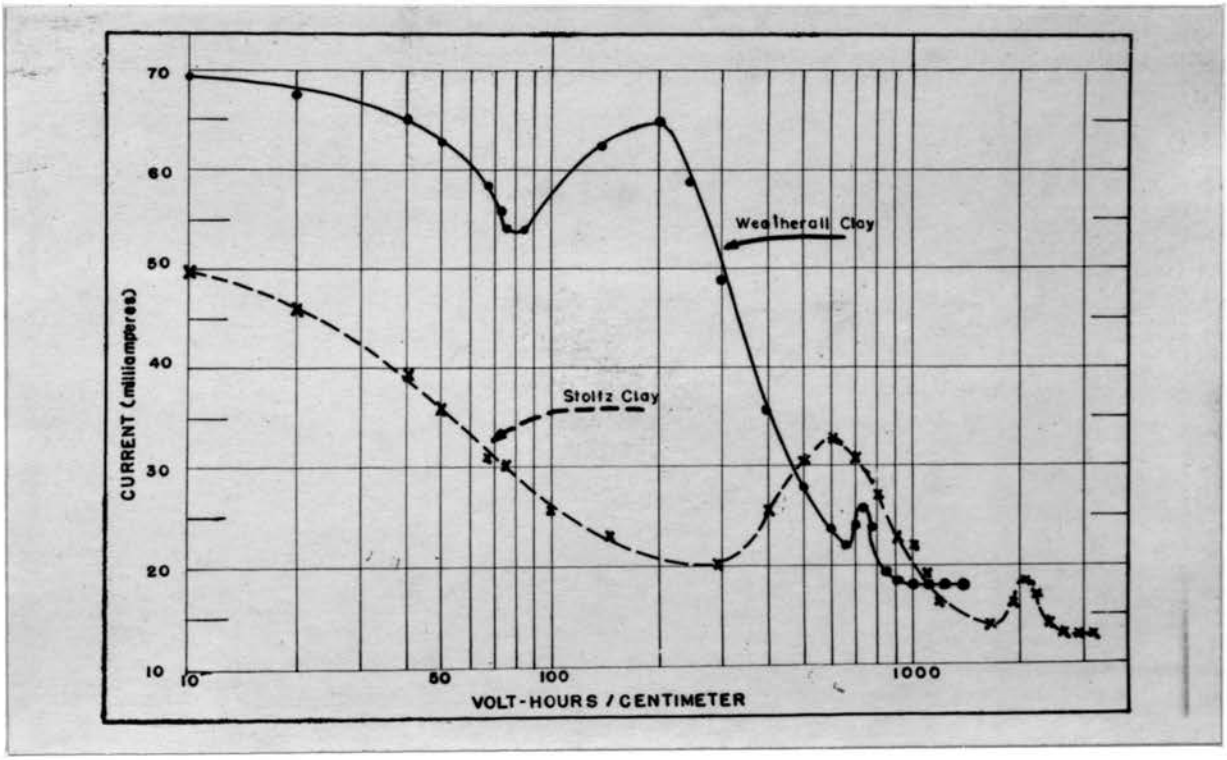

Figure 12.

Electrodialysis Time-Current Curves for Weatherall Clay and Stoltz Clay.

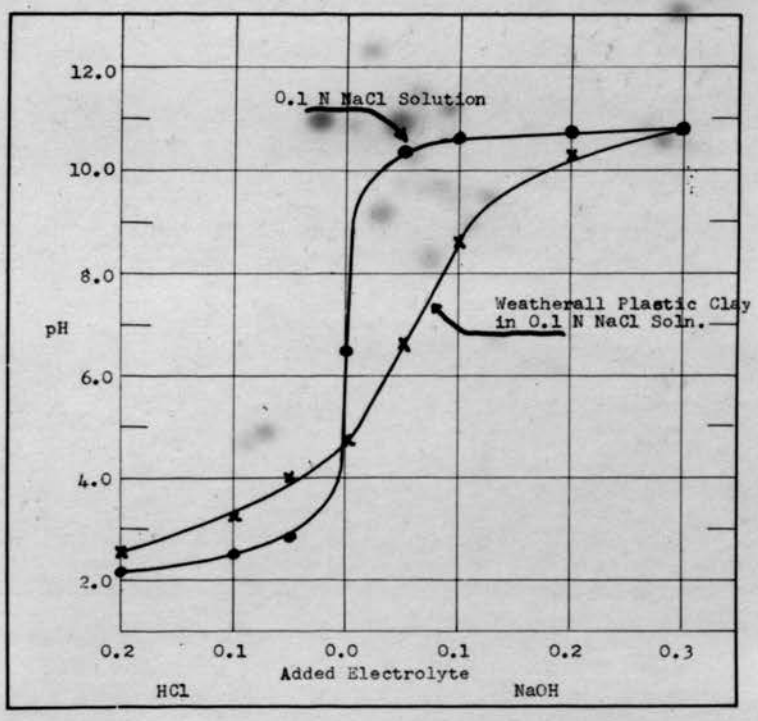

Figure 13.

pH Curves for Determination of Base Exchange of Weatherall Plastic Clay.

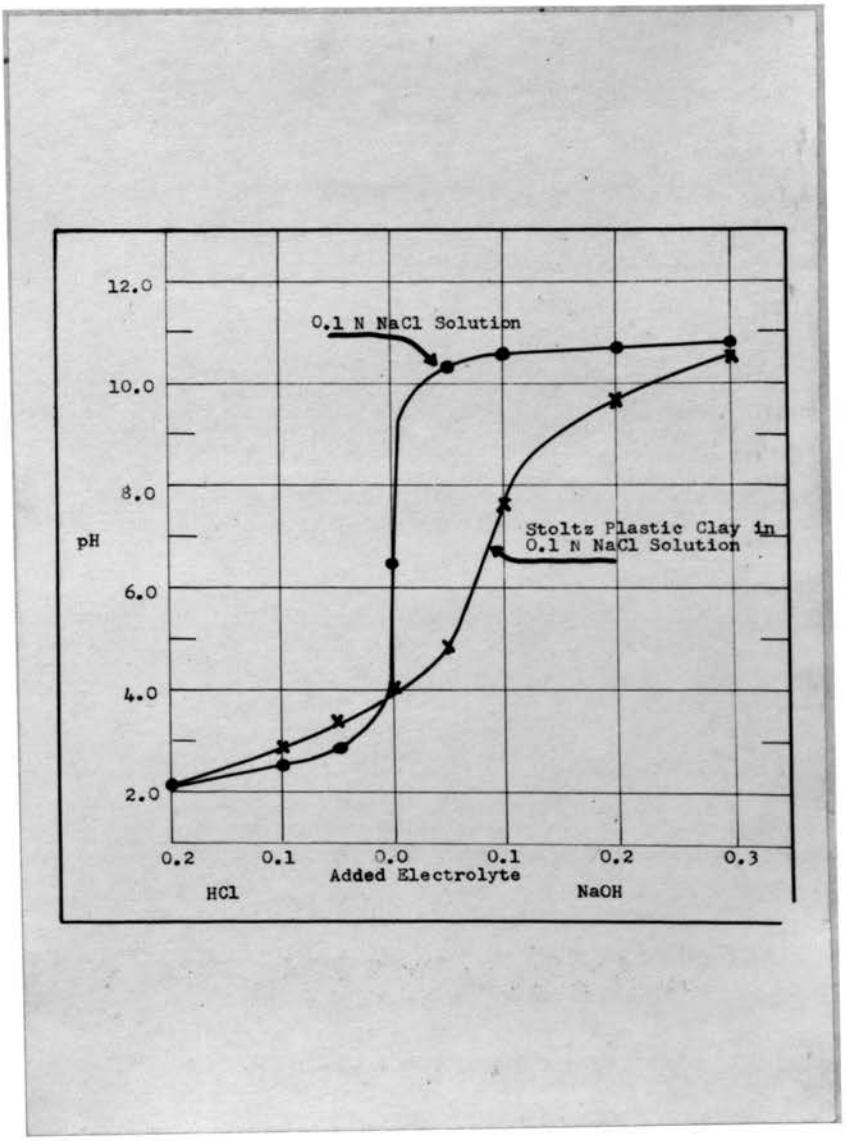

Figure 14.

pH Curves for Determination of Base Exchange of Stoltz Plastic Clay.

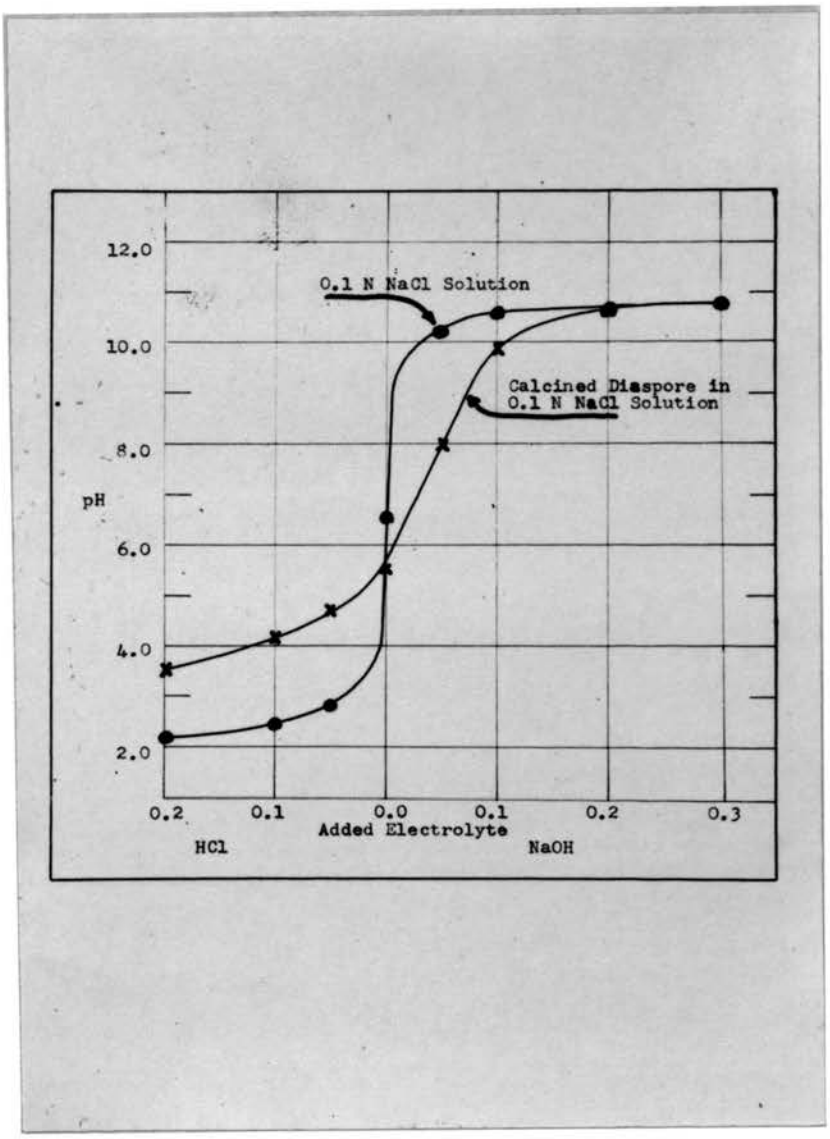

Figure 15.

pH Curves for Determination of Base Exchange of Calcined Diaspore Clay.

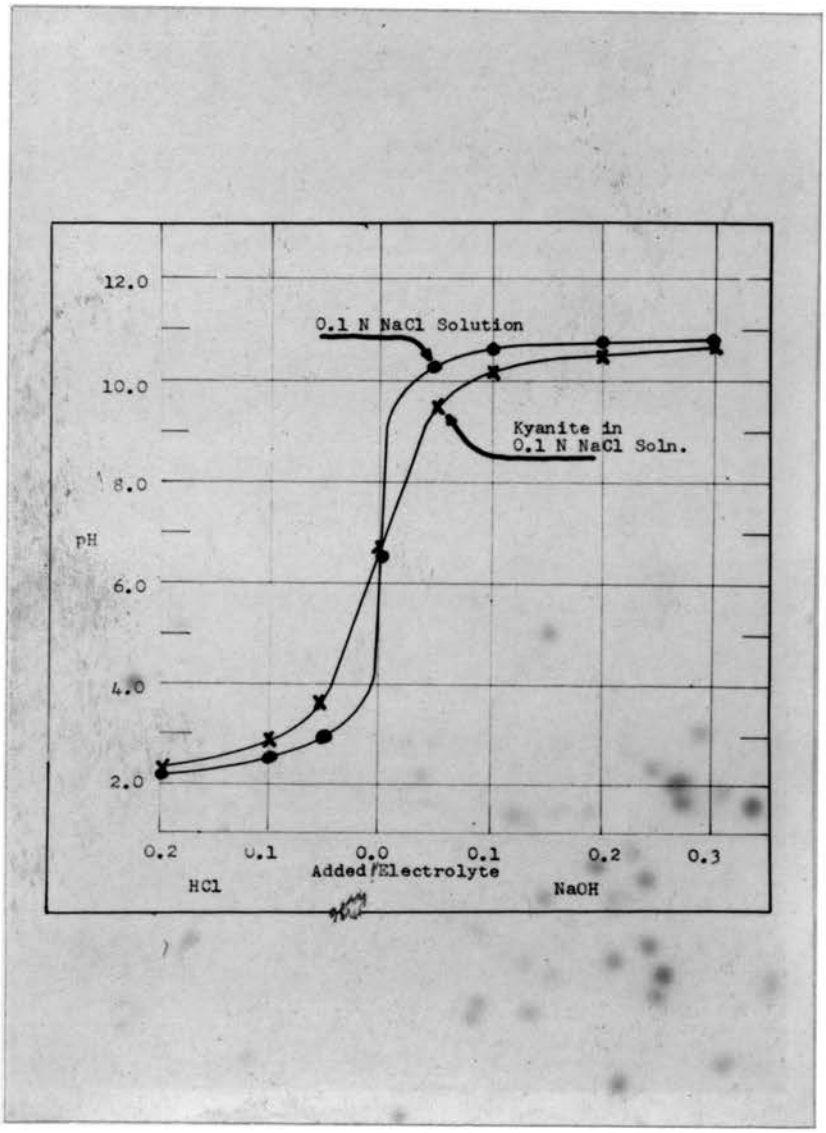

Figure 16.

pH Curves for Determination of Base Exchange of Kyanite.

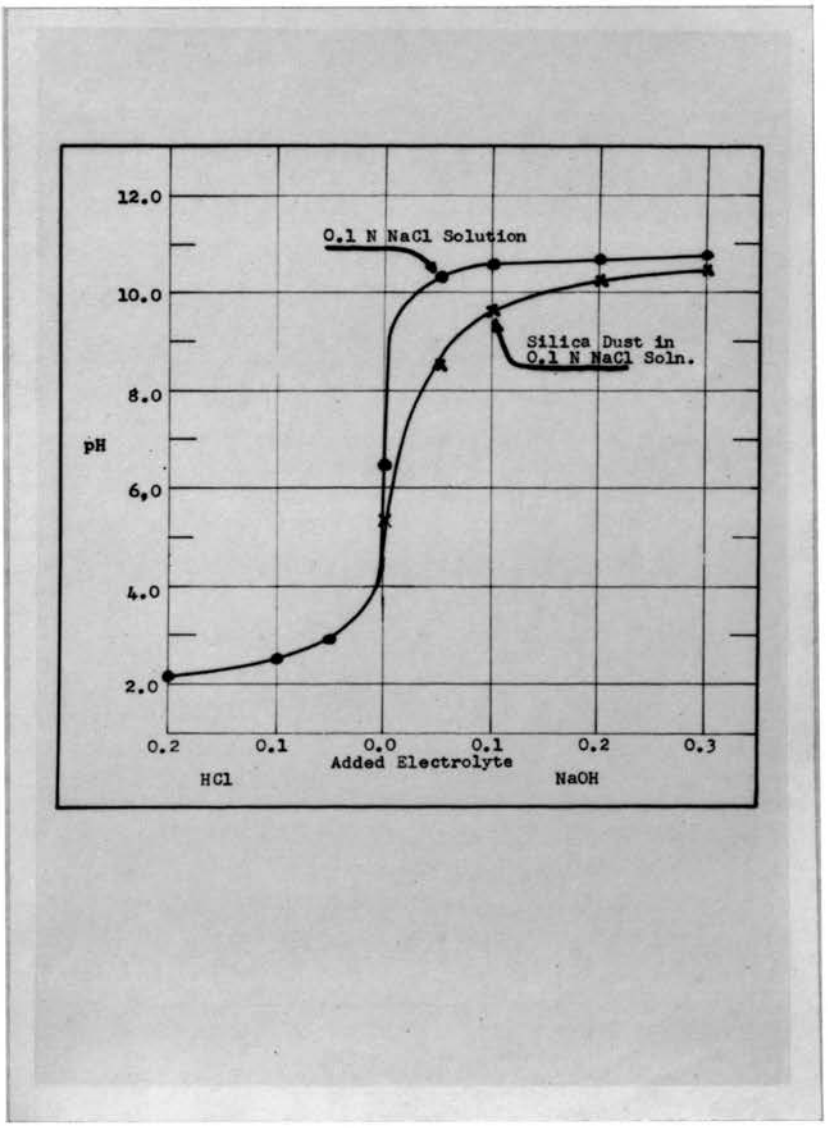

Figure 17.

pH Curves for Determination of Base Exchange of Silica Dust.

TABLE VI.

BASE EXCHANGE CAPACITIES (pH = 7.0)

Weatherall clay	5.6
Stoltz clay	8.1
Calcined diaspore	2.7
Kyanite	0.3
Silica dust	1.2

These figures, then, showed that the base exchange capacity of the Stoltz clay was about 40% higher than that of the Weatherall clay, which was indicated by the current curves in Figure 12.

It was felt that the decreasing current at the beginning of each dialysis indicated the removal of the ions of the soluble salts present. The first increase in current, then, was probably due to the removal of the more loosely held monovalent ions adsorbed on the surface of the clay particle while the second peak was due to the removal of the polyvalent ions. An attempt was made to determine whether this was true by analyzing the cathode effluents.

Since the concentration of ions in these effluents was so small, normal methods of analyses were not considered. Instead, the flame photometer was employed. This instrument is used for the rapid determination of sodium, potassium andother metals in dilute solution. It measures quantitatively the intensity of one of the principle spec-

trum lines of the desired element since the intensity of the flame is proportional to the concentration of ions or atoms injected into the flame.

The Perkin Elmer Flame Photometer, Model 52A, used in this work, is an emission spectrometer combined with a flame source and a photoelectric detection system for measuring the intensity of the flame. The output meter of the instrument reads in proportion to the light intensity emitted by the flame. The instrument was first calibrated with solutions of known concentration by obtaining the photometer reading and plotting that against the concentration.

After these curves were obtained for all elements desired (Figures 18 and 19), the unknowns were run, one element at a time, and the photometer reading recorded for each. The concentration of the unknown was then obtained from the standard curve for that particular element.

This equipment was not available in this department and these tests were run elsewhere. The blue-sensitive photocell, used in the determinations of calcium and magnesium, was not available so that only sodium and potassium were reported.

The electrodialysis of the clay to obtain these effluents was performed in the small cells and the voltage was kept relatively low in order to keep the current as low

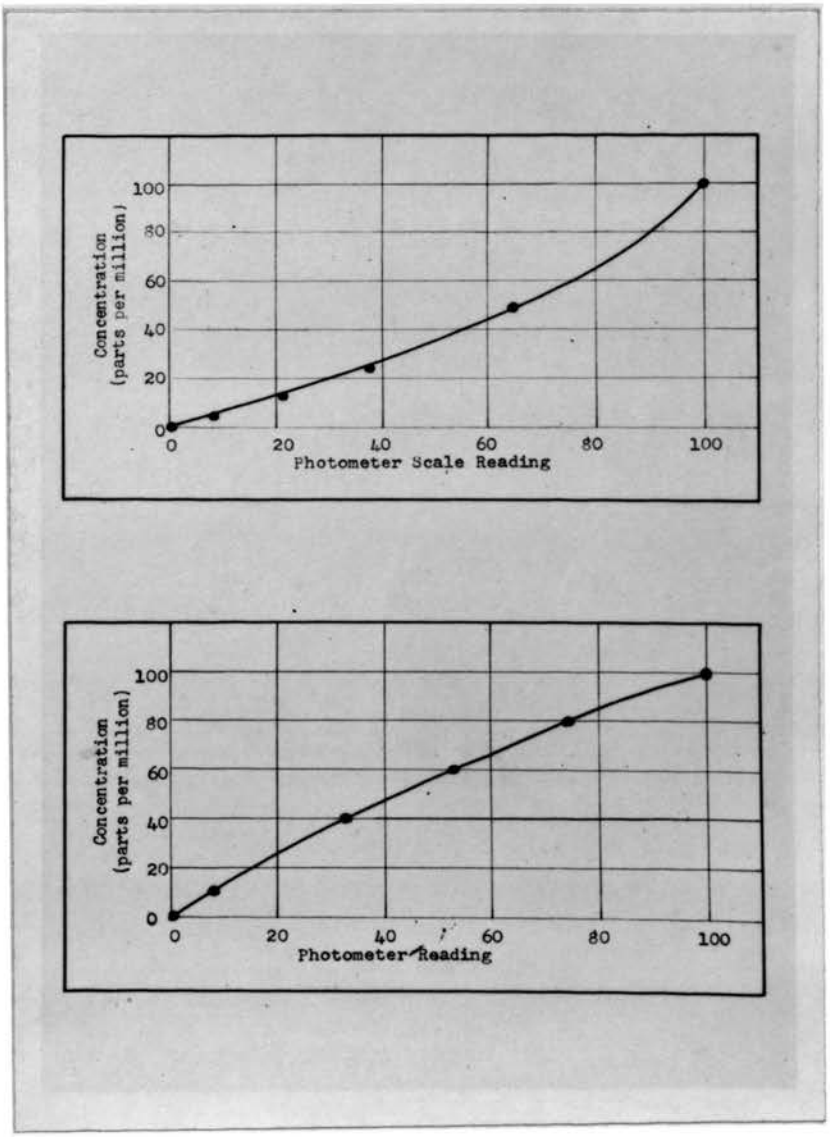

Figure 18 (above).

Standardization Curve for Determination of Sodium with Flame Photometer.

Figure 19 (below).

Standardization Curve for Determination of Potassium with Flame Photometer.

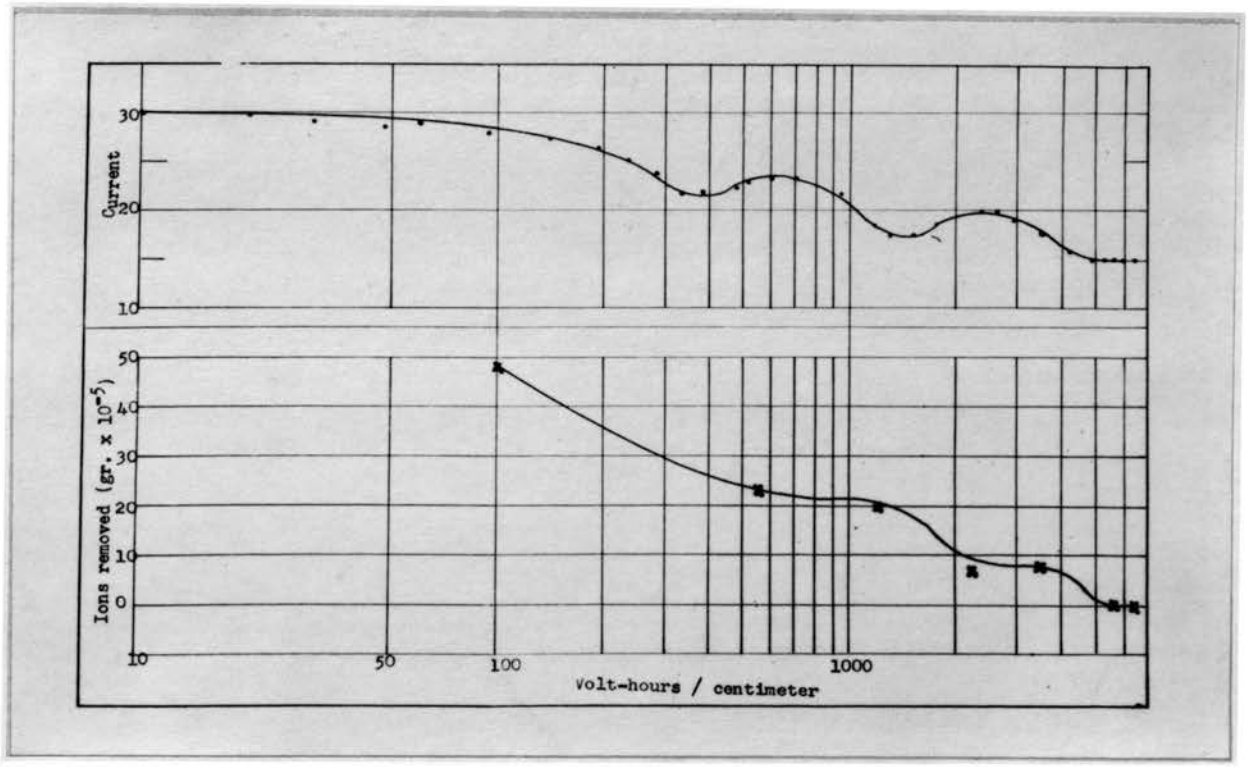

Figure 20.

Relation of Amount of Ions Removed by Electrodialysis to Time-Current Curve.

as possible. The effluents were retained in such a manner that the determination of ion concentration would correspond to the various peaks of the time-current curve. The total volume of each effluent sample was measured, then the liquid evaporated to about 200 ml. A corresponding volume of the distilled water used was evaporated to 200 ml and analyzed to determine the amount of sodium and potassium present. The results of the flame photometer determinations of sodium and potassium in the Weatherall clay are shown in Table VII.

TABLE VII.

FLAME PHOTOMETER ANALYSIS OF EFFLUENTS OBTAINED BY ELECTRODIALYSIS OF WEATHERALL CLAY*

Sample Number	Time (hrs.) From	To	Na Concentration ($\times 10^{-5}$ grams)	K Concentration ($\times 10^{-5}$ grams)
1	0	1	1.80	7.20
2	1	31	10.50	29.40
3	31	97	7.50	13.75
4	97	164	10.20	10.20
5	164	183	5.80	5.80
6	183	266	3.80	5.70
7	266	312	2.35	2.35
8	312	360	0.00	0.00
Total	0	360	41.95	74.40

*These figures do not include Na and K present in water.

From this, the total exchangeable and soluble sodium and potassium was calculated to be 1.16% of the total weight of the clay. The total sodium and potassium present in the Weatherall clay, as given by the chemical analysis,

was 1.64%. The comparison of the current curve and the amount of alkaline ions removed is shown in Figure 20. It was not intended that the bottom curve of Figure 20 should be interpreted as indicating the actual rate of removal, but rather the relative removal of the ions. The points marked "x" along this curve are center points of the period over which the effluent samples were removed.

It was believed that this indicates that a method along these lines could be devised to determine the exact order and amounts in which the ions are removed. Although this had but little to add to the present study, due to the fact that the concentrations of calcium and magnesium could not be determined, it seemed academically proper to mention this fact here.

After dialysis, the clays were dried, ground, and blunged in 2 N. NaOH for 48 hours. The clay was permitted to settle out, the supernatent liquid siphoned off and more distilled water added. After settling, the top liquid was again removed. This was repeated until the pH of the wash water removed was not more than 8.0. The clay slip was then run through a Sharples Super Centrifuge using sufficient flow and speed to retain all of the clay on the liner. The clay was then dried, reblunged with distilled water, and run through the centrifuge again. The resulting sodium clay was then dried and ground.

A standard solution of $Ca(OH)_2$ was prepared and sufficient of this added to the clays to give the desired amount of calcium to replace the sodium. After addition of the calcium ions, the clays were washed and centrifuged in the same manner as given in the preparation of the sodium clays. Sodium clays with 0.5, 1.0 and 4.0 milliequivalents of calcium per hundred grams were prepared. The clays were analysed for sodium and calcium and the results shown in Table VIII.

TABLE VIII.

ALKALINE AND CALCIUM CONTENT OF PREPARED CLAYS

(a) Weatherall

	Raw Clay	H-Clay	Na-Clay plus 0.0 Ca	1.0 Ca	4.0 Ca.
Sodium & Potassium	1.64	1.30	2.29	2.06	1.36
Calcium	.75	.51	.50	.55	.55

(b) Stolts

Sodium & Potassium	1.46	—	1.63	1.34	1.11
Calcium	.80	—	.53	.56	.56

Mix "Bx" was used to prepare mortars from these clays. The workability was tested immediately after mixing and again after three weeks storage. The results are given in Figure 21.

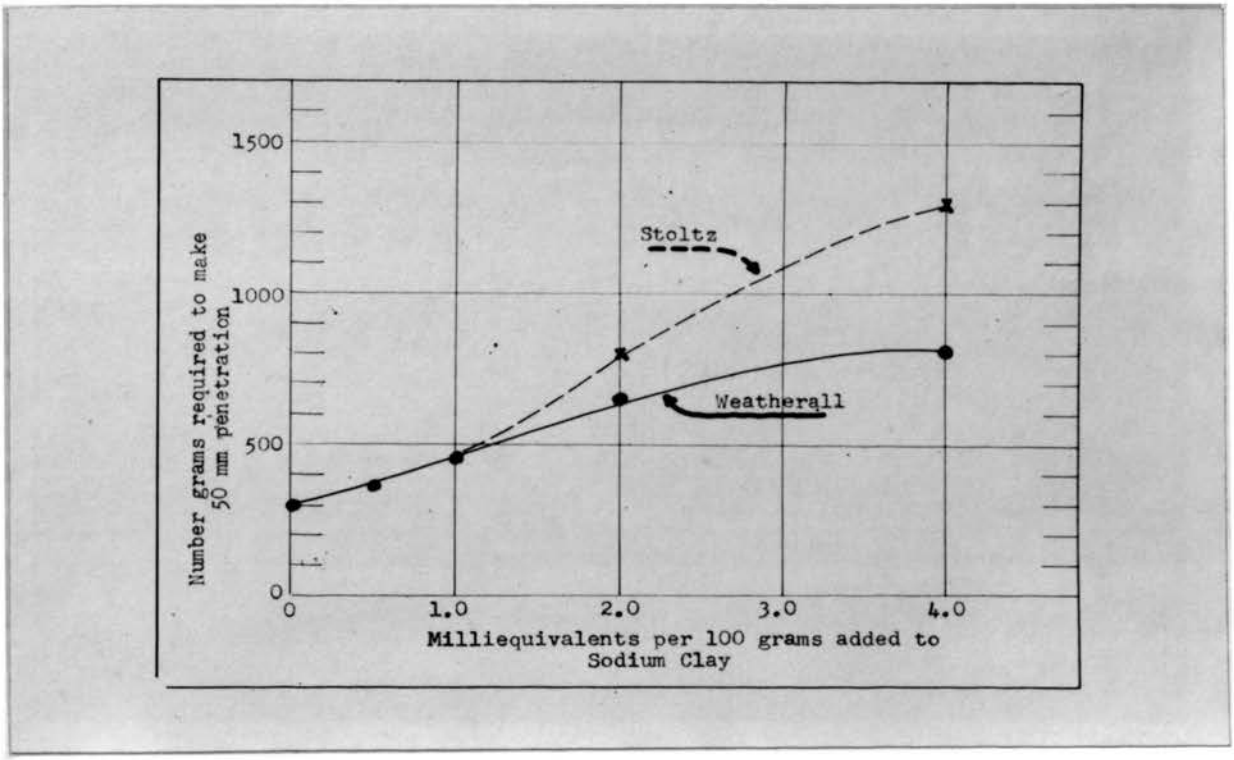

Figure 21.

Workability of Mortar "Bx" versus Added Exchangeable Ions.

CHAPTER VIII.

EFFECT OF MINERAL CONSTITUENTS OF CLAYS

The mineral composition of the two clays was first determined using differential thermal analysis and x-ray diffraction patterns. The chemical analysis of the two clays showed a considerably greater amount of free silica present in the Weatherall clay than in the Stoltz clay. This could not be determined by differential thermal analysis if the silica was present as quartz since the endothermic peak of quartz at 575° C. would be superimposed by the 590° C. endothermic peak of kaolinite, the latter being much more intense.

Differential thermal curves were obtained for two of the four types of Weatherall clay (Figure 22) and Stoltz clay (Figure 23) used in the work described in the preceding chapter plus hydrogen clay. The endothermic peak at 800° was originally thought to be due to the calcite present in both clays. A sample of sodium Weatherall clay was calcined at 500° for 18 hours, then thoroughly leached to remove any carbonates that may be present. The differential thermal curve obtained from the resultant material (Figure 22, e) still showed a slight endothermic peak around 800°.

A sample of pure opal was obtained and the differ-

ential thermal curve of this material (Figure 24, a) showed a large number of endothermic peaks, one of the more intense being at about 800°. A curve of chemically pure silica gel (silicic acid) was obtained (Figure 24, b) and it revealed just one intense endothermic reaction at 130°. The curve of the silica dust used in this study showed not only the quartz transformation at 575° but also additional endothermic peaks, one of which occurred at 800°.

A synthetic mixture was prepared based on the mineral constituents calculated from the chemical analysis of Weatherall clay. The differential thermal curve obtained from this sample (Figure 24, e) showed a marked resemblance to the curve obtained from the hydrogen Weatherall (Figure 22, b) except that the typical kaolinite peaks at 580° and 980° were much more intense for the former.

The x-ray diffraction patterns obtained using the North American Philips X-Ray Spectrometer (Figures 25 and 26) showed plainly the difference between the free silica content of the two clays. Some of the calcite peaks were present but they were generally lost in the kaolinite and quartz patterns. Copper radiation was used to obtain these patterns.

It may be noted here that Tha Hla[57] and Roy[58] have claimed to have disintegrated micas by electrodialysis. The x-ray patterns of the two clays shown here do not indicate any such process having taken place during the electrodialysis of these two predominantly kaolinitic clays.

Several penetration tests were run in connection with this phase of the study. A mixture was made consisting of 40% silica gel and 60% sodium silicate and water. This composition was used to obtain the same consistency of the mortars after mixing. This mixture was tested, sealed and tested again 24 hours later. Another mixture was made to the proper consistency using 63% silica dust and 37% sodium silicate and water. This was also tested and sealed then re-tested after 14 and 21 days storage at room temperature.

A mortar was made using Georgia Kaolin and varying amounts of silica dust and these also were tested for gelation. The results of these tests are shown in Figure 27.

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57 Tha Hla, op. cit., p. 139.

58 Rustrum Roy, "Decomposition and Resynthesis of the Micas", Journal of the American Ceramic Society, 32: 202-09, 1949.

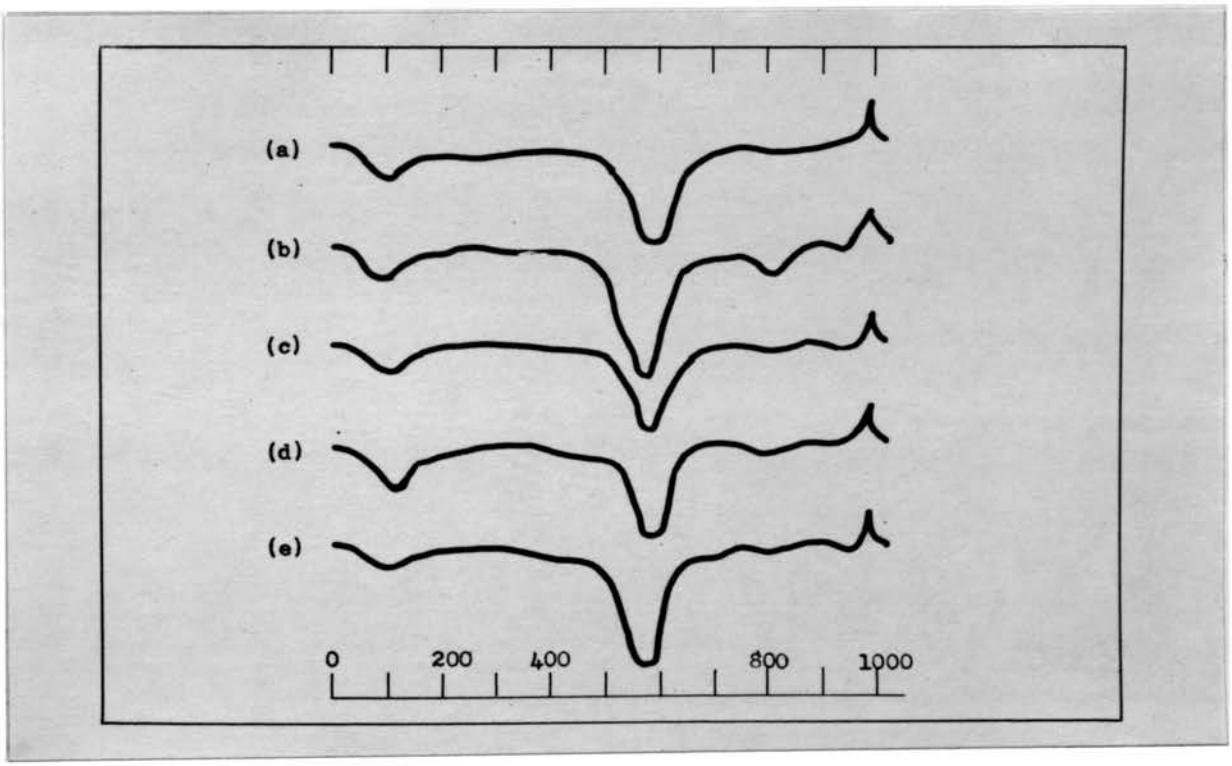

Figure 22.

Differential Thermal Curves for Weatherall Clay

(a) Raw clay
(b) Hydrogen clay (electrodialyzed)
(c) Sodium clay
(d) 4.0 me. Ca/100 gr. clay added to sodium clay
(e) Sodium clay calcined at 500°C for 18 hours and leached with H_2SO_4

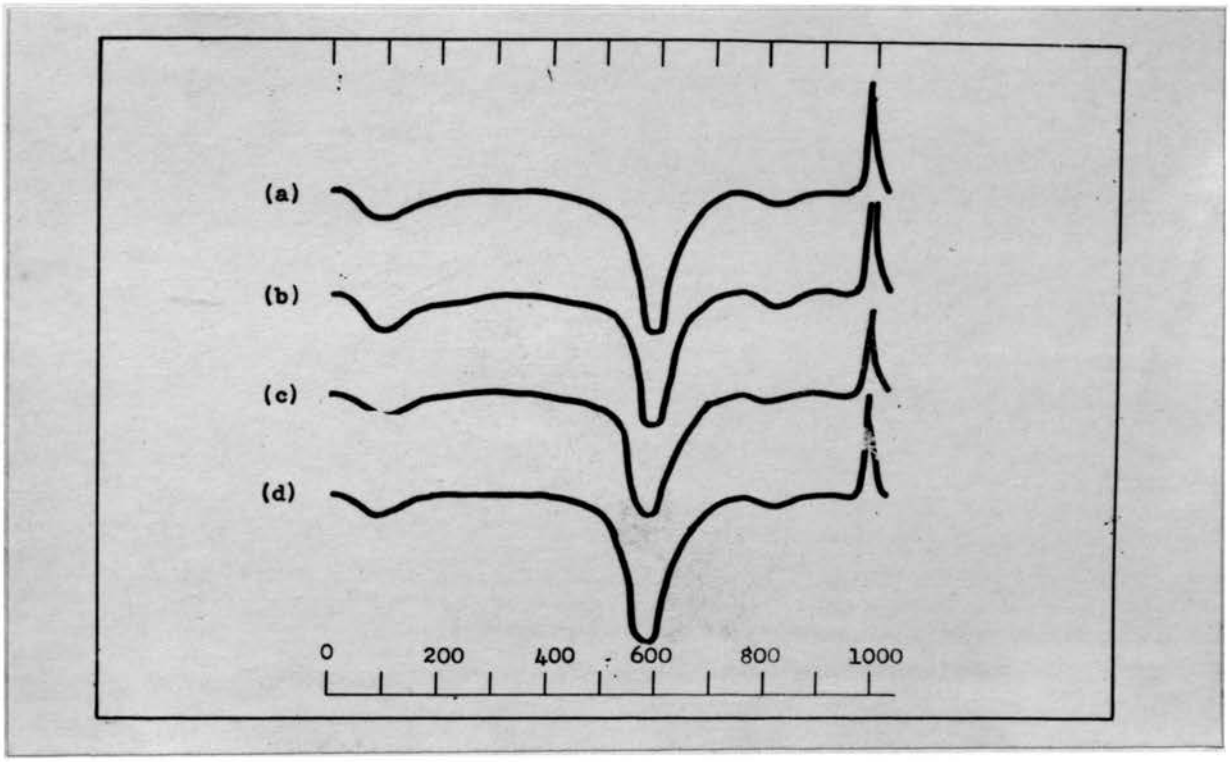

Figure 23.

Differential Thermal Curves for Stoltz Clay.

(a) Raw clay
(b) Hydrogen clay
(c) Sodium clay
(d) 4.0 me. Ca/100 gr. clay added to sodium clay

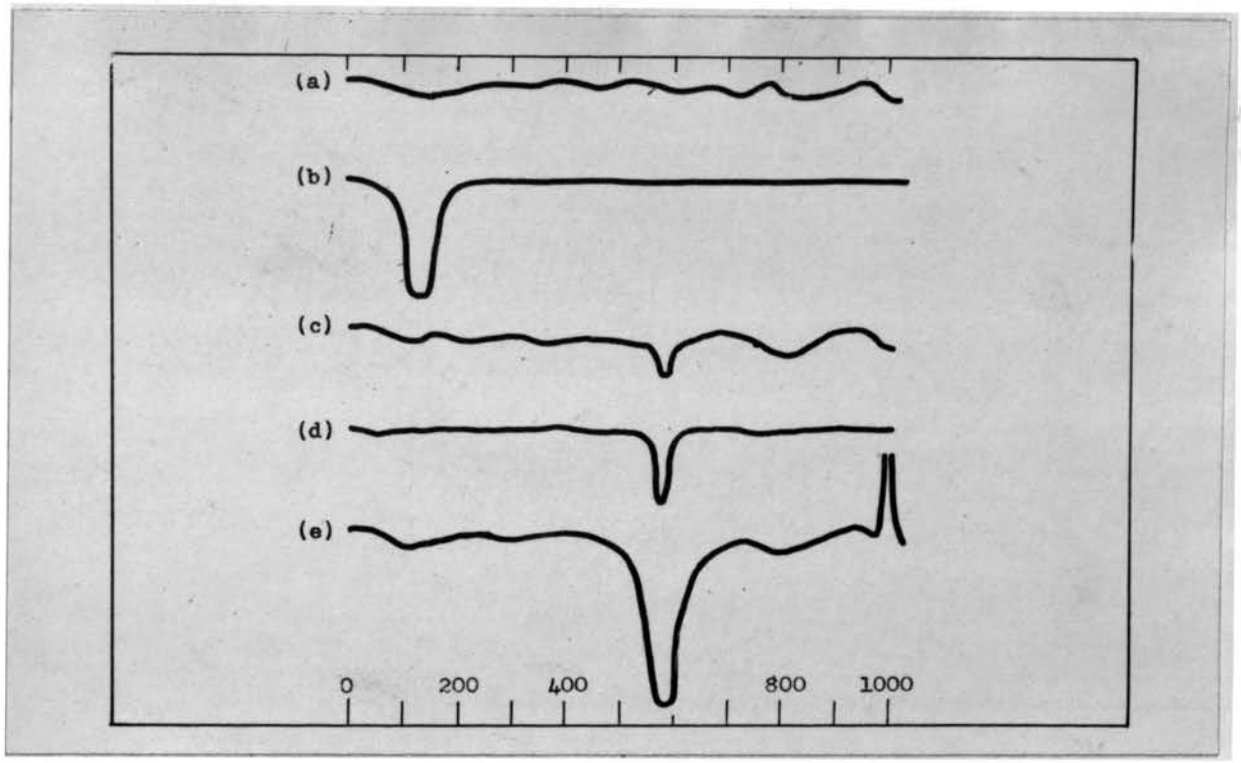

Figure 24

Miscellaneous Differential Thermal Curves

(a) Opal
(b) Silicic Acid (silica gel)
(c) Silica dust (300 mesh)
(d) Potter's flint (quartz)
(e) Synthetic mix—72% Georgia kaolin
21% Potter's flint
7% Opal

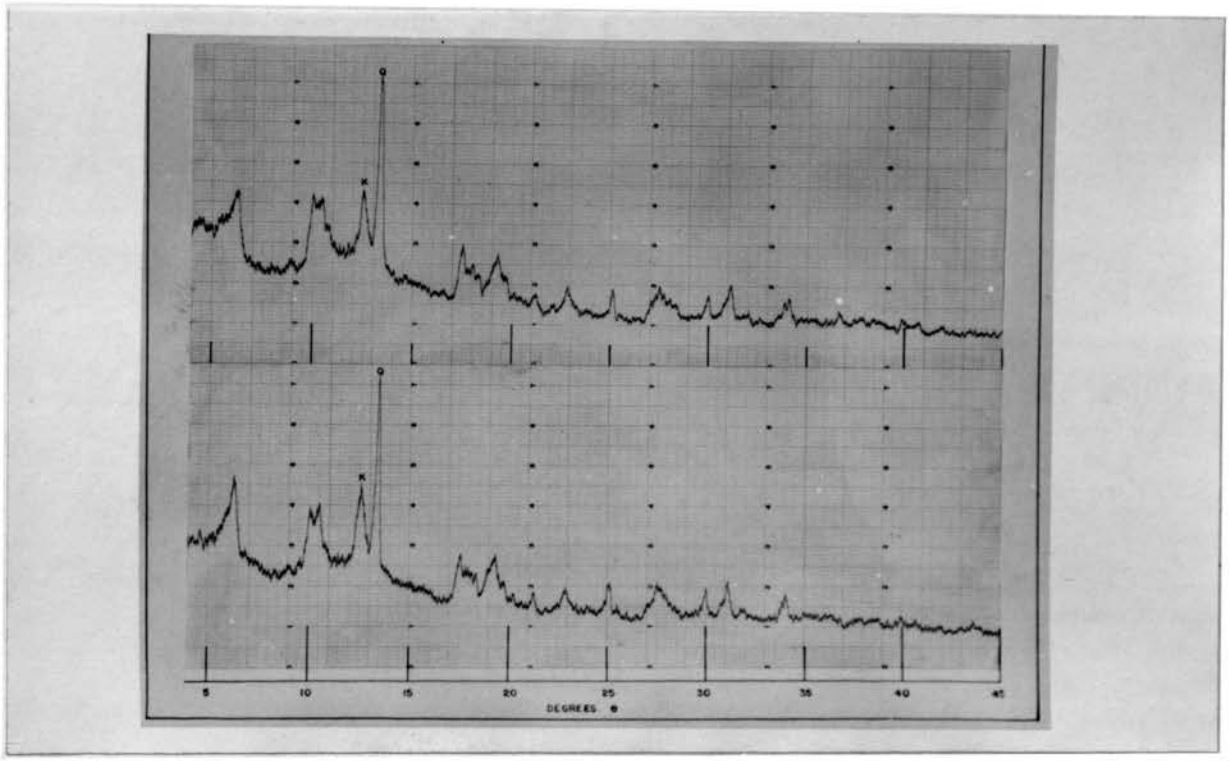

Figure 25.

X-Ray Diffraction Patterns of Weatherall Clay before (below) and after (above) Electrodialysis.

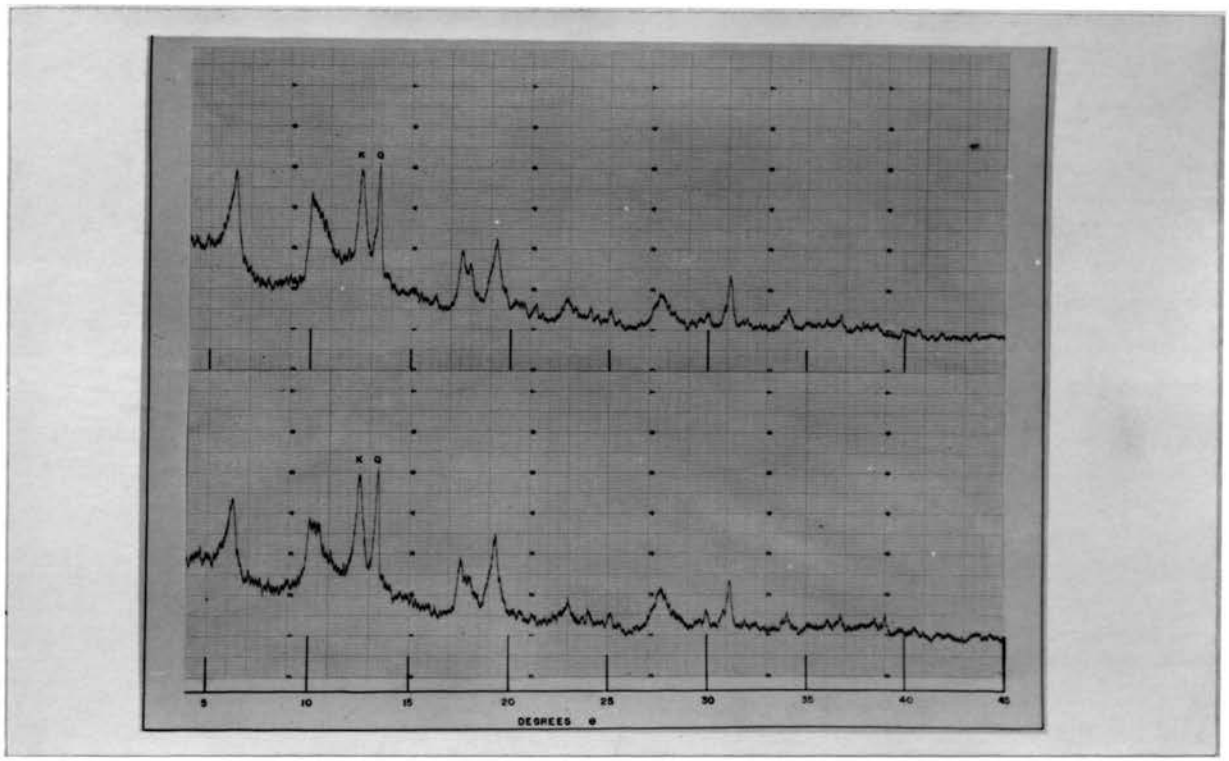

Figure 26.

X-Ray Diffraction Patterns of Stoltz Clay before (below) and after (above) Electrodialysis.

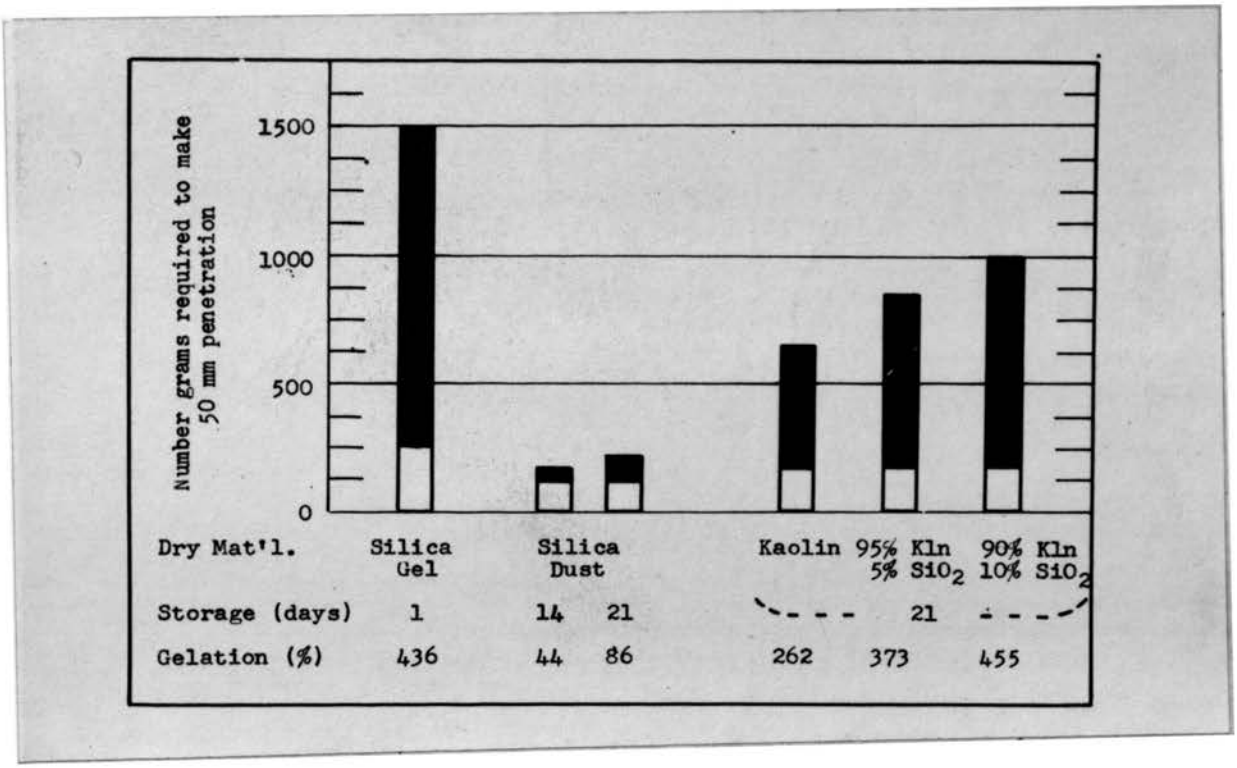

Figure 27.

Effect of Silica on Workability.

CHAPTER IX.

DISCUSSION OF DATA

I. DIFFERENT MIXES AND MATERIALS

There seemed to be little doubt from the results obtained that the three mixes ("A", "B" and "C") had different workability characteristics. The clay was common to all three mixes, diaspore was present in "A" and "B" only and kyanite was present in "B" and "C" only. The tests run on the effect of silica in a mix (described in Chapter VIII) did not indicate that it was a major factor in the gelation, although it did make a contribution. During the electrodialysis of kyanite, it was found that, if the kyanite was not washed with ether or hydrogen peroxide, the current increased considerably after the first few hours and the pH of the center compartment decreased. This was thought to be due to the retaining of some of the floatation reagents by the kyanite--possibly an amine. If one of these large-molecule compounds was used, the organic radical could not pass through the membrane of the dialysis cell and the current would remain high. This reagent, then if present on the kyanite, might protect the clay colloid from reaction with the sodium silicate. This was thought to be one possible explanation of the difference in the

workability of the three mortars.

The use of the two clays made a decided difference in the gelling property of mortar "B". The Stoltz clay imparted a greater fluidity to the mortar immediately after mixing than did the Weatherall clay, but, after 10 days storage at room temperature, the workability of the mortar using the Stoltz was less than that using the Weatherall. The possible reasons for this will be discussed later in this chapter.

By omitting the bentonite from mortar "B", the workability was greatly improved but the omission did not remedy the situation. The use of bentonite as a suspending medium in the mortar seemed to be somewhat unnecessary as the mortar at the end of four weeks had not settled out. The mortar might possibly be agitated sufficiently during shipment to cause the settling out, but the gain derived there by using bentonite would probably be overcome by the increased gelation caused by its presence in the mortar.

II. Admixtures.

Of all the admixtures testing in the mortars, none seemed entirely satisfactory. Several of these, namely, washed casein, sodium alginate (Keltex), and sodium carbonate, showed their value in decreasing the gelation to or near a satisfactory degree. But, as stated, each had its

own particular disadvantage.

The washed casein was not deemed economically feasible to add to the mortar as the increase in cost of the product could not be adsorbed by the manufacturer and it was not felt that the additional workability of the mortar would be worth the difference in price to the consumer. The sodium alginate was acceptable from the point of view of arresting the gelation, but it introduced sodium ions into the mortar which would, naturally, result in a lowering of its refractoriness. Some of the other alginates were also tested, although not reported, and none of these showed the improvement noted by using the Keltex.

If the sodium ion of the alginate was beneficial, then the addition of the sodium in some other form should also help. This was suggested by earlier workers and the sodium carbonate was added in this study just as a matter of comparison. It should be pointed out that the weight required to make the desired penetration in the mortars with sodium carbonate was the same as that required in the mortar using the sodium alginate. This indicated rather conclusively that the sodium ion rather than the algin caused the decrease in the gelation.

An additional interesting point was the fact that the two mortars, "B" and "Bx" both had the same consistency after storage when the sodium was added to the original

batch.

The addition of the two aluminum salts greatly increased the gelling of the mortar giving proof to the statement that a heavy metal salt would increase the hardening.

III. Adsorbed Ions

As has been pointed out, the Stoltz clay seemed to cause an increase in the gelation of the mortars. The base exchange capacity of this clay was found to be about 40% higher than that of the Weatherall clay. Of course, this fact alone should not be termed the cause of the hardening. There must be sufficient polyvalent cations present to cause hardening, although, in clay with a high base exchange capacity, there may be sufficient monovalent cations present to overcome this gelation if the number of polyvalent cations is low.

The known presence of relatively large amounts of exchangeable calcium and magnesium in the bentonites was considered to be the reason for the increase in the hardening of the mortar with increasing bentonite content. If the current-time curves obtained from the electrodialysis of the clays can be considered a measure of the relative amounts of monovalent and polyvalent ions, then the Stoltz clay would be expected to have more of the latter adsorbed. It was regrettable that the equipment was not available to

study more thoroughly the ion content of the effluents from dialysis. Certainly more study should be made of this as it would, with the proper controlling and recording equipment, give a simple means of determining whether or not a clay had too many polyvalent ions adsorbed to be used in an air-setting mortar.

The presence of these exchangeable ions was believed to have contributed to the hardening in two ways. If the adsorbed calcium, for instance, was replaced by the sodium from the sodium silicate, the calcium ion released would join with the free silicate ion to form a calcium silicate which is the product formed so extensively in chemical grouting. It is also possible that the base-exchange capacity of the clay is not fully satisfied with adsorbed ions, in which case, the sodium ions from the sodium silicate would satisfy this vacancy, or charge, and reduce the soda-silica ratio of the silicate. This in turn would increase the viscosity of the mass, as it would have the same effect as using a sodium silicate of higher ration, which has been found to be undesirable.

The results obtained by adding given amounts of calcium to the sodium clays were felt to be indicative of the amounts of polyvalent ions that could be tolerated in the clays. The Stolts clay, having the higher base exchange capacity, was able to adsorb more calcium, which acceler-

acted the hardening. The results indicated that the exchangeable bases present on the clays were a powerful factor in the mechanism of the hardening as the sodium clay with no calcium added had excellent workability after storage and the percent gelation was less than 100 for both clays.

The fact, as previously mentioned in this chapter, that the Stoltz clay imparted greater fluidity to the mortar immediately after mixing than did the Weatherall clay was thought to be due to the presence of a greater amount of plastic kaolinite in the former. The relatively high amount of free silica present in the Weatherall clay would tend to decrease the plasticity of the mortar when mixed. After the ten day storage period, the gelation imparted by the adsorbed ion on the two clays undoubtedly overcame this and the workability of the two mortars was reversed.

IV. Mineral Constituents

The very fact that the Weatherall clay contained so much more free silica, a material of low base exchange capacity, would account to some degree for the lower base exchange capacity of the clay.

The results obtained by mixing free silica with a relatively pure kaolinite in a mortar indicated that an increase in the silica content of the mixture would play a

role in the hardening mechanism. It is known that amorphous forms of silica, of which opal is one, react more quickly than do crystalline forms.[59] The fact that the Weatherall clay contained some opalline material indicated that its presence might have had some effect on the gelation. The differential thermal curves seemed to indicate that the silica dust may have had some of this material present, but the gelation tests do not indicate that it (the silica dust) had any major effect on the hardening. The rapid manner in which the silicic acid hardened was felt to be indicative of the hardening of mass in which any large amount of the sodium was removed from the silicate.

The differential thermal curves failed to reveal the presence of illite in either clay. If this mineral was present in a clay, the base exchange capacity of the clay would be higher than if it were not present, and there would probably be more exchangeable polyvalent cations available. This would have a definite effect on the hardening of the mortar.

The presence of calcite in both clays was not believed to have much, if any, effect on the gelation due to its relative insolubility. Over long periods of time, how-

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59 A. B. Searle, "Refractory Materials", (London, Chas. Griffin and Company, Ltd., 1924), pp. 134-35.

ever, it might have some effect.

CHAPTER X.

CONCLUSIONS

From the results of this investigation, the following conclusions have been drawn:

1. The gelation, or hardening, of an air setting refractory mortar out of contact with air was due to the formation of a thixotropic gel, the exact cause of which was not traceable to any single reaction.

2. The most predominant single factor for this gelation was found to be the presence of polyvalent exchangeable cations adsorbed to the clay or other dry materials used in the mortar. The total base exchange capacity of the clay must also be considered. One way of overcoming this would be in the selection of clays so that the amount of exchangeable polyvalent ions would be small.

3. The addition of soluble salts of monovalent elements decreased the gelation of a given mortar. The use of a sodium clay gave similar results, but, since these elements usually act as a flux, they reduced the refractoriness of the mortars.

4. The addition of some protective colloids were found to retard the gelation to a satisfactory degree but, in most cases, the increased cost of the mortar was not deemed economically advisable.

5. The presence of free silica was found to be a contributing factor to the gelling of the mortar, although the base exchange characteristics of the clays and other materials overshadowed this. Any soluble heavy metal salts, including the sulfides, would increase the hardening of the mortar.

6. The use of bentonite as a suspending medium in the mortar was found to be detrimental to the workability of the mortar. The bentonite, with its high base exchange capacity and high percentage of exchangeable magnesium was found to increase the gelation considerably and was not used in the mortars employed in the latter part of this work.

7. The time-current curves obtained during electrodialysis seemed to be indicative of the relative amounts of monovalent and polyvalent ions present. This is based on the analysis by the flame photometer of the effluents obtained from the dialysis. The analyses were made for only sodium and potassium and a much better check should be made by analysing for calcium and magnesium, chiefly, with the flame photometer method.

8. The use of graphite anodes was not satisfactory for electrodialysis cells as they began to disintegrate after a period of usage and caused a great increase in the current flow. This might be mistaken for the removal of

adsorbed ions. Aluminum was found to be fairly satisfactory for anodes, but, in time, they too eroded, although no perceptible change in current was noted. Platinum was found to be the most satisfactory anode material.

9. X-ray diffraction patterns taken of the clay before and after electrodialysis did not show any evidence of the disintegration of the kaolinitic clays used in this study. This should be expected since the lattice of the kaolinites are more rigidly bound together than are those of the montmorillinites or micas that have been found by other investigators to disintegrate during electrodialysis.

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